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GEOLOGY AND PETROGRAPHY OF THE BEZWADA AND KONDAPALLE HILL RANGES

Part II. Charnockites and Associated Rocks and Chromite*

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Introduction

In an earlier paper the author (1946) detailed the results of his field and laboratory investigations on the para-gneisses (khondalites) of the Bezwada-Kondapalle area. In this paper the results of the study of charnockites occurring in association with the khondalites and granite-gneisses at Kondapalle are described.

The hypersthene-bearing granular rocks of the Archaean complex of South India were designated as 'Charnockite Series' by Sir T. H. Holland (1900) and as they ranged from acid to ultrabasic in composition were regarded by him as the different phases of crystallisation of a normal plutonic magma. Similar rock types more or less identical in their mineral suites, textures and field relationships were also observed and studied in India by Ghosh (1941), Jayaram (1910–13), Crookshank (1938), Hallowes (1934), and Ramarao (1945) and also described by Adams (1929) from Ceylon, Groves (1933) from Uganda, Gevers and Dunne (1943) from South Africa, and Stillwell (1918) and Prider (1945) from Australia.

Mode of Occurrence, Association and Distribution

In the Kondapalle range acid and intermediate charnockites occur as huge massifs and the basic and ultrabasic varieties as dykes intrusive into the khondalites or as transitional products of the acid and intermediate varieties. A point of special interest in the charnockites of the Kondapalle area is the occurrence of chromite as lenses and veins in the basic and ultrabasic members. Such association has not so far been reported from any charnockite region.

The several minor ranges of hills extending from Ibrahimpatnam (80° 32′, 16° 35½′) in the south to 16° 41′ in the north are all composed of

* Contributions from Geology Department, Andhra University, Waltair.

acid charnockites with transition to intermediate varieties. There is an intimate association of these with pink banded granite gneiss. In many places minor stringes of granite gneiss could be seen ramifying into charnockites. There is considerable intermingling between the two and though no distinct intrusive evidence of the pink gneiss could be traced anywhere, it appears to be later than the charnockites. A marked feature noted in the acid and intermediate varieties of charnockites in the area is the presence of distinct banding; alternate bands showing concentrations of mafic and felsic minerals. This banding seen on fresh surfaces persists even on the weathered rock. The basic and ultrabasic charnockites which, as pointed earlier, are limited in their distribution are represented by norites, biotite norites, garnetiferous basic charnockites, hornblende-hypersthene-granulites and pyroxenites. A norite dyke with a width of about ten feet was traced for about two furlongs, till concealed by talus and soil, cutting the khondalites in the ·245 hill, almost at right angles to the strike of khondalites, with contact effects. A similar mode of occurrence of the basic and ultrabasic charnockites is prominently seen in the hill north of Ibrahimpatnam which consists of norites and mica norites grading into pyroxenites. These basic and ultrabasic rocks also occur in association with intermediate and acid varieties with transitional relationship in many localities here. Often, the transitional zones from type to type are so well marked as to be seen as distinct bands for long distances. In a charnockite quarry which is close to mile 2/4 on the forest road can be seen the gradation of an acid charnockite from the top through intermediate variety to norite and then to pyroxenite at the bottom. All these are having a rough N-S run. A similar type of occurrence is to be seen in the pit about 100 yards east of the forest road near mile 2/0 and also in the excavations for chromite on the western flank and near the southern edge of the ridge ·1086 containing the peak ·1086.

Lastly the occurrence of some garnetiferous basic charnockites in the hill near mile 1/6 on the forest road and also in the other hills in the same range has to be mentioned. Hornblende-hypersthene-granulites are seen in the low mound opposite mile 1/3 on the Ibrahimpatnam-Kondapalle road. All the types of rocks discussed above are here and there seen cut up by several pegmatites and quartz veins.

Mineralogy

The mineral assemblage in the series of rocks is varied. In this section the characters of the various minerals are described, the interrelationship of the minerals in the different rock types being relegated to the section on

petrography. The minerals studied here are blue quartz, felspars, pyro xenes, amphiboles, micas, garnets, magnetite, ilmenite, apatite and chalcopyrite.

Quartz.—The mineral is abundantly present in the acid charnockites and sparingly in the intermediate varieties and is conspicuous by its absence in the others. In hand specimens, it has invariably a bluish or slightly greyish blue colour. In thin section, it is seen to contain several minute needle-like inclusions and exhibits features as strain shadows, wavy extinctions and brecciation which can be attributed only to mechanical forces. Most of the grains are quite fresh but some are turbid. In some acid charnockites, small rounded blebs of quartz of varying sizes are found intergrown with microperthite suggesting a myrmekite texture; also, vermicular quartz with acid plagioclase is common.

Felspars.—In the hand specimens, felspars are light grey in colour. In all types of charnockites, except in pyroxenites, the felspars preponderate over all the minerals combined. In acid types microcline-microperthite predominates, while in intermediate and basic varieties, the plagioclase varies from andesine to calcic labradorite. The few grains of plagioclase in pyroxenites are acid bytownite. The plagioclases are generally twinned, untwinned grains being not rare. Strain effects, such as bent twin lamellæ and undulose extinctions are commonly met with in the feldspars. This is in conformity with the observations of Crookshank (1938) on the charnockites of the Eastern Ghats, of which this is but the southern limit.

The composition of the plagioclase feldspars and the twinning law obeyed by them were determined on the Federov Universal Stage. The anorthite content of the feldspars is found to vary from 75 to 10 per cent. The plagioclases exhibit predominant twinning on (010) as the composition plane of different twin lamellæ, with Albite and Albite-Carlsbad laws occurring frequently.

The composition of plagioclase can also be deduced from the chemical analysis of the rock if the *k* and 2 *alk*/*al*+ *alk* values are plotted in Niggli's diagram. It will be seen from the diagram (Fig. 1) that the nature of plagioclase deduced from the chemical composition of the rock agrees fairly well with optical determinations. From a study of the diagram it is evident that the plagioclases show a gradual variation in anorthite content from the acid to the ultrabasic charnockites.

Hypersthene.—Hypersthene is an essential constituent of the charnockites. In hand specimens, it is identified by its greenish brown colour and prismatic habit. In polarised light, it varies from colourless and pale pink to

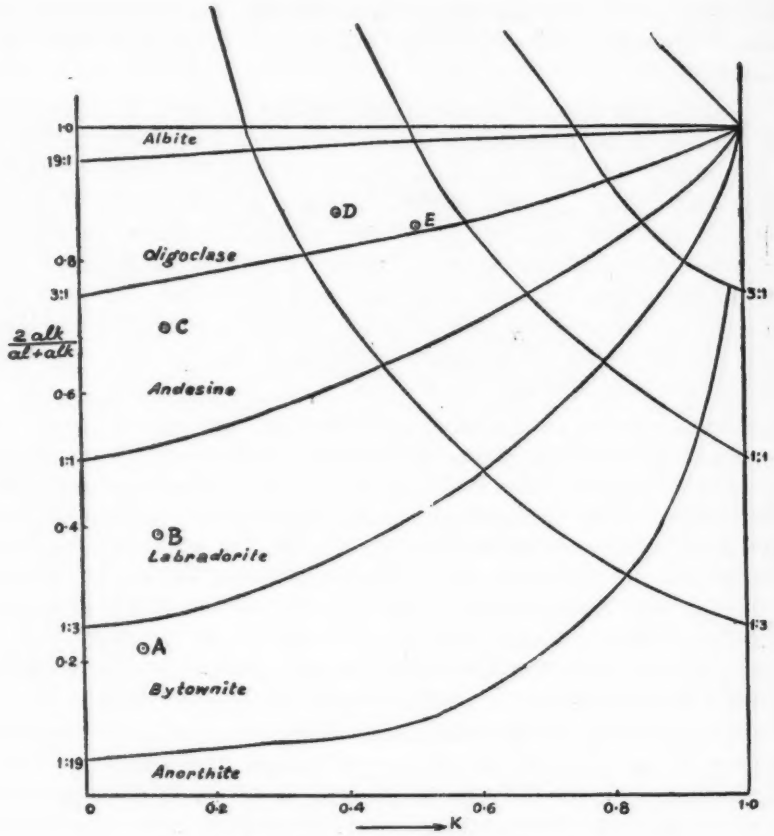

FIG. 1. $K - \frac{2\ alk}{al + alk}$ Diagram for the charnockites and granite gneiss.

green. The former (presumably the more magnesic type) is associated mostly with the ultrabasic charnockites—pyroxenites; while, the pink to green type (presumaby the more ferruginous variety), with the other types of rocks.

The colourless variety resembles enstatite in the lack of pleochroism but the determination of the optic axial angle of the mineral on the Federov Stage yields a value of 2V ranging between 70° and 75° with X as the acute bisectrix, thus definitely proving it to be a rather magnesian variety—bronzite.

The commonest variety, however, is the coloured one occurring as granular clusters and coarse prisms. It exhibits pleochroism in the usual shades of:—

X and Y: Bright pink: Z: bluish green to greyish green. Schiller inclusions are common. The mineral is negative and the optic axial angle is almost the same in the different grains (2V= 60–62°). Generally, in the colourless variety extinction is found to be parallel to the vertical cleavage traces, but in the coloured variety, the extinction is inclined, the inclination reaching a maximum of 33° (K/16). This feature has been noted in the hypersthenes of charnockites of several other areas. Several explanations have been offered for such oblique extinctions by Sen Gupta (1916), Groves (1933), Washington (1916), Chatterjee (1939), Hess and Phillips (1938), Johansen (1938), Naidu (1943) and Ray and Roy (1945).

The mineral is often intergrown with garnet and iron ores and on alteration is converted, in some cases, into an yellowish green amphibole.

To determine the composition of this hypersthene, a small patch of the mineral in norite was carefully isolated and freed completely from admixed matter by Thoulet solution, and the magnetite separated by electro-magnet. The powder was then chemically analysed, the results of which are shown along with the analyses of hypersthenes given by different workers from other localities, in Table I.

From Table I it is clear that the hypersthene of the Kondapalle charnockites, like the one from St. Thomas Mt., Madras, is a slightly aluminous variety. It compares also well with the aluminous hypersthene of Uganda charnockites and Bidalotite from Mysore.

The computation of the formula of the mineral is done by the simplest method of calculating the relative proportions of the different oxides of bivalent, trivalent and quadrivalent elements. Then Al and Fe‴ are put together, Fe″, Mn and Mg are grouped together, Ca separately expressed, so also *si.* The formula of the hypersthene can be expressed as follows:

$5\,(Al, Fe''')_2O_3,\ 27.5\,(Fe, Mn, Mg)\,O,\ CaO,\ 36\,SiO_2$

The compositions of the different rhombic pyroxenes are represented in a trilinear co-ordinate diagram (Fig. 2) adopting the Q, L, M values. A perusal of this diagram clearly discloses that the hypersthene of the Kondapalle charnockites shows a very slight abnormality. If it had been a normal pyroxene it would have had the position of the point P ($M_{75}\,Q_{25}$), but since the projection point of this hypersthene, as well as the points of all others, fall slightly away from the point P and towards Q, it is evident that the hypersthene is slightly more siliceous and contains normative quartz. We come to the same conclusion from a purview of the results of

TABLE I

Analyses of Rhombic Pyroxenes

	I	II	III	IV	V	VI
SiO_2 ..	51·69	56·91	55·15	53·16	48·44	53·60
Al_2O_3 ..	5·95	6·10	6·50	10·55	7·91	3·51
Fe_2O_3 ..	1·26	1·90	2·10	4·30	0·33	0·79
FeO ..	23·09	18·87	17·68	17·10	20·88	11·38
MnO ..	0·42	0·64	0·34	nil	0·92	0·19
MgO ..	16·40	14·42	16·62	11·95	19·35	25·34
CaO ..	1·44	1·62	1·58	nil	1·44	4·19
Na_2O ..	..	..	..	tr.	..	0·25
K_2O ..	..	..	..	..	..	0·03
H_2O ..	..	..	..	..	..	0·27
H_2O ..	..	..	..	2·00	0·08	0·04
TiO_2 ..	..	..	0·03	1·35	undet.	0·29
Total ..	100·25	100·46	100·00	100·41	99·35	99·88
			Niggli values			
si ..	103·1	127·3	117·0	127·8	90·0	97·4
al ..	6·9	8·0	8·4	14·8	8·5	3·7
fm ..	90·0	88·0	87·9	85·2	88·7	87·7
c ..	3·0	4·0	3·7	..	2·8	8·2
alk ..	..	..	..	..	..	0·4
ti ..	..	..	..	2·4	..	0·4
mg ..	0·55	0·57	0·61	0·53	0·61	0·79
Q ..	28·5	35·6	33·4	38·2	25·0	24·8
L ..	4·3	5·2	4·9	..	4·4	6·1
M ..	67·2	59·2	61·7	61·8	70·6	69·1

I. Hypersthene from norite, Kondapalle; Analyst: M. Sriramarao.

II. Hypersthene from charnockite, St. Thomas Mt., Madras; Analyst: C. Rajagopalan, *Proc. Ind. Acad. Sci.*, 1946, **24**, No. 3.

III. Hypersthene from charnockite, Uganda; Analyst: A. W. Groves, *Q. J. G. S.* (Lond.), 1932, **91**, pt. 2, p. 152.

IV. Bidalotite, Analyst: Chemist, M.G.D., *Proc. Ind. Acad. Sci.*, 1937, **5**, No. 6, p. 222.

V. Hypersthene from gabbro, Se 1/4 Sec. 20, T. 65, N. R. 4 W, Minnesota, Analyst: E. A. Schneider, *Jour. Geol.*, **3**, p. 1.

VI. Orthopyroxene from Bushveld, *Amer. Min.*, 1938, **23**, 453.

chemical analysis wherein the silica percentage instead of being exactly 50, exceeds that figure.

From the above studies it is quite clear that the hypersthene from Kondapalle, which is optically negative, is not clinohypersthene or pigeonite, both of which are positive. It is truly orthorhombic and the inclined extinction in some sections appears to be really due to a section of the pyramidal face as has been suggested by Johansen (1937).

Augite.—This is a minor constituent of the charnockites and is present in most of the types, occurring as isolated accessory grains. It is only in

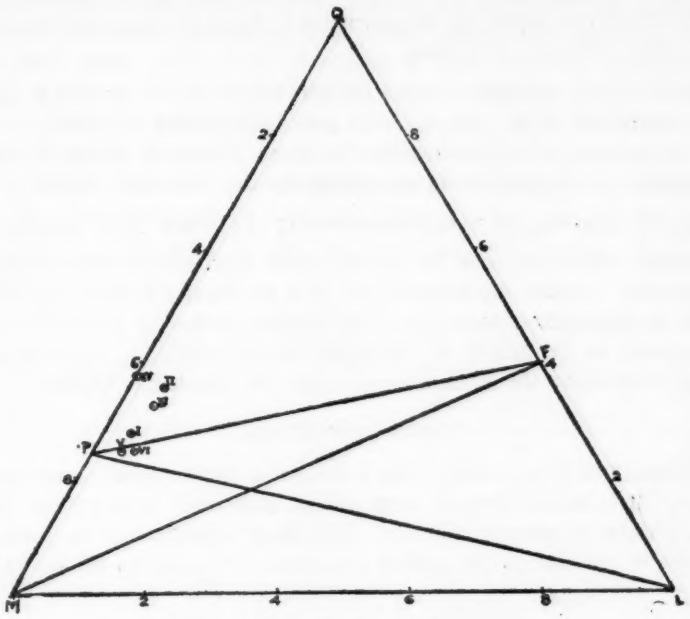

FIG. 2. Q L M Diagram for Pyroxene.

the norites that it is present in small amounts, though it is not absent in the acid, intermediate and ultrabasic varieties. It is greenish black in colour and has a prismatic habit.

In thin section, it is green in colour corresponding to the green tint in the Z direction of vibration of its associated hypersthene. Its optic axia angle varies from 54° to 59° with Z as acute bisectrix and the variation in the angle between Z and *c* (Z*c*) is from 42° to 53°. The mineral alters into green hornblende.

Hornblende.—Next in importance among ferromagnesian minerals occurring in the charnockites is hornblende. It is generally granular, though coarse prismatic plates are not uncommon. The prismatic cleavage is well developed. It is intensely pleochroic with

X: Bright yellow; Y: Greenish brown; Z: Dark green.

The mineral is optically positive, the optic axial angle (2V) varying four degrees on either side of 74° and the extinction angle (Z*c*) varying between ° and 11°.

Its secondary origin is clear from the fact that in many cases it occurs in irregular forms replacing the pyroxene in large patches, only rare 'islets' of the latter mineral remaining.

Biotite.—The mineral is deep reddish brown in colour and is found as small scales and laths. In the acid and intermediate charnockites it is a reaction product of hypersthene. In some norites it is the chief mafic constituent. It is pleochroic according to the following scheme:

X: Brown; Y: Reddish brown; Z: Very dark brown.

Garnet.—Garnets, pink in colour, were prominently seen in the basic charnockites. Under the microscope, they are faintly pinkish and occur as clusters or aggregates, sometimes poikilitically enclosing vermicular quartz. They appear to be mostly of secondary origin, replacing hypersthene and forming rims with the liberation of silica as vermicular quartz.

Minor Constituents

Opaque Iron Ores.—Magnetite is found in all the rocks as an accessory mineral. It is in the form of large grains, sometimes with crystal contours and sometimes in granular clusters. It is fairly abundant in the norites and decreases in amount as the acidity increases. It seems to be highly titaniferous.

Apatite.—Under the microscope, the mineral is easily identified as narrow laths, with high refractive index and characteristic grey polarisation colours.

Chalcopyrite.—This is noticed in one or two sections of norites and is recognized by its brass yellow colour in reflected light.

Chromite.—The mineral in the form of minor, thin stringers is noticed at the contacts of pyroxene grains in pyroxenites.

Petrographic Description and Chemical Analyses of the Charnockites and Granite Gneiss

It was already pointed out that the charnockites in this area are represented by acid, intermediate, basic and ultrabasic varieties and that they sometimes show transitional relationship. Representative samples of the four types were studied optically and by chemical methods:

A. *Pyroxenite* (*Pyroxenitisch*).—The ultrabasic type is represented here by pyroxenite. Megascopically, it is a medium-grained, holocrystalline, equigranular rock, dark green to apple green in colour. It shows a variation in specific gravity from 3·30 to 3·38.

In thin section, the rock is seen to consist almost exclusively of rhombic pyroxene. Monoclinic pyroxene and basic plagioclase are very minor constituents, never collectively exceeding 3 per cent. by volume. The pyroxene is in some places completely serpentinised, as distinguished by the bastite pseudomorphs. The complete alteration of the rock has sometimes resulted in a talc-schist. A few small flakes of chlorite are observed. The titaniferous magnetite and chromite are the accessory minerals.

As pointed out earlier, the pyroxene which is the essential constituent of this rock is really bronzite and the rock, strictly speaking, is hence a bronzitite.

TABLE II

Analyses of Pyroxenite and Allied Rocks

	A	A_1	A_2	A_3	A_4
SiO_2 ..	50·22	55·27	54·64	46·86	47·44
Al_2O_3 ..	7·81	4·13	2·52	9·80	5·36
Fe_2O_3 ..	1·87	0·45	2·10	16·35	3·13
FeO ..	7·05	7·17	6·76		12·42
MnO ..	0·25	0·03	0·25	..	0·15
MgO ..	27·28	28·36	30·01	18·08	19·96
CaO ..	2·96	2·93	2·51	9·57	7·60
Na_2O ..	0·63	0·86	0·18	trace	0·48
K_2O ..	0·10	0·18	0·15		0·10
TiO_2 ..	0·56	0·16	0·75	..	1·29
P_2O_5 ..	0·06	..	0·04	..	0·27
Cr_2O_3 ..	0·30	..	..	..	0·07
FeS_2 ..	..	0·17	..	..	..
H_2O ..	0·61	0·30	0·58	..	0·34
H_2O ..	0·04	0·04		0·67	0·08
Total	99·74	100·05	100·49	101·33	98·69
		Niggli values			
si ..	87·0	100·0	96·0	85·0	88·0
al ..	8·0	4·5	2·5	10·5	5·5
fm ..	85·0	88·0	92·0	71·0	66·5
c ..	6·0	5·5	5·0	18·5	27·0
alk ..	1·0	2·0	0·5	..	1·0
ti ..	0·7	0·2	0·9	..	1·6
k ..	0·09	0·12	0·33	..	0·11
mg ..	0·87	0·88	0·90	0·69	0·75

A . Pyroxenite from the big chromite quarry, Kondapalle, Analyst: M. Sriramarao.

A_1. Hypersthenite, Norseman, Western Australia, Analyst: Simpson, *Bull. West. Aust. Geol. Surv.*, 1906, **21**, 119.

A_2. Bronzitite, New Caledonia, Analyst: Boiteau, *Compt. Rend.*, 1911, **152**, 820.

A_3. Hypersthenite from Pallavaram near Madras, Analyst: T. L. Walker, *Mem. G. S. I.*, 1900, **28**.

A_4. Bahiaite, Pammal Hill, Pallavaram, Madras, Analyst: H. S. Washington, *Amer. Jour. Sci.*, 1916, **41**, 325.

The modal composition of the rock determined by Shand's Recording Micrometer is as follows (figures per cent.):—

Pyroxene (orthorhombic and monoclinic)	94·0
Hornblende	1·9
Chlorite	0·8
Plagioclase	0·5
Opaque Ores	3·6

The rock was chemically analysed and the results are recorded in Table II, column A. For purposes of comparison analyses of similar rocks from other areas are given in the same table.

The Basis Composition of the rock is shown below:—

Kp	0·32
Ne	3·19
Cal	8·44
Sp	2·08
Fo	53·29
Fa	7·91
Fs	1·92
Q	22·18
Ru	0·35

The Kata-Molecular Norm and C.I.P.W. Norm are arranged in Table III.

TABLE III

	Kata-Molecular Norm	C.I.P.W. Norm
Or	0·53	0·55
Ab	5·32	5·24
An	14·07	14·73
C	..	1·33
Cord	3·81	..
Hy	47·56	50·20
	6·20	8·84
Fo	17·62	11·90
Fa	2·30	2·45
Mt	1·91	2·78
Il	..	1·06
Cr	0·32	0·45
Ru	0·35	..
H_2O	..	0·65
	100·00	100·18

An examination of the norms and mode of this rock discloses some interesting features. No free olivine was met in the rock; but, it is present

abundantly in the normative composition. This is easily explained by the assumption that it has combined with silica to form pyroxenes. Likewise the corundum and cordierite of the norms appear as aluminous hypersthene. The normative plagioclase is bytownite having 73 per cent. anorthite. This value corresponds closely with the Universal State determinations and to the one deduced from the $k-2\ alk/(al+alk)$ diagram of Niggli (Fig. 1).

B. *Norite* (*c-gabbroid*).—The most common basic rock in these charnockites is norite. It is medium to coarse-grained and granular and is dark grey in colour.

TABLE IV

Analyses of Norite and other Basic Rocks

	B	B_1	B_2	B_3	B_4	B_5
SiO_2 ..	50·28	53·20	53·82	53·05	50·62	50·11
Al_2O_3 ..	18·08	12·53	8·07	8·91	16·45	14·31
Fe_2O_3 ..	2·10	3·29	2·11	3·26	2·61	2·00
FeO ..	9·28	14·17	7·00	9·52	7·02	11·38
MnO ..	0·36	0·12	0·21	0·09	..	0·31
MgO ..	7·02	1·08	18·39	14·42	6·61	7·64
CaO ..	9·34	6·58	5·96	6·76	9·23	11·52
Na_2O ..	2·38	2·73	1·28	0·66	3·04	2·37
K_2O ..	0·53	2·37	0·82	0·48	1·42	0·16
TiO_2 ..	0·80	1·91	0·33	1·77	1·77	0·84
P_2O_5 ..	0·30	0·16	0·04	0·09	0·39	tr
H_2O ..	0·08	1·68	1·57	0·65	0·18	0·31
H_2O ..	0·03	..	0·08		0·37	0·06
CO_2 ..	..	..	0·05	..	..	..
Total ..	100·58	99·82	99·73	99·66	99·71	101·01
			Niggli values			
si ..	117·0	155·0	112·3	116·9	124·0	109·4
al ..	24·5	21·5	9·9	11·6	24·0	18·3
fm ..	46·5	46·0	73·1	70·4	43·0	49·5
c	23·0	20·5	13·3	15·9	24·0	27·1
alk ..	6·0	12·0	3·7	2·1	9·0	5·1
ti ..	1·5	3·6	0·6	3·1	3·2	1·3
p ..	0·3	0·1	..	..	0·4	..
k ..	0·12	0·36	0·30	0·32	0·23	0·02
mg ..	0·56	0·10	0·78	0·67	0·56	0·51

B. Norite from quarries near Ibrahimpatnam, Analyst: M. Sriramarao.

B_1. Upper norite, Tautesboogte, Middleburg Dt., Analyst: J. Jacob, *Trans. Geol. Soc. S. Africa*, 1932, **35**.

B_2. Coarse norite from the central part of the dyke east of Durgarpur, Keonjhar, Analyst: P. C. Roy, *Rec. G. S. I.*, **71**, 112.

B_3. Augite norite from Eriyur, S. Arcot Dt., Analyst: P. Bruhl, *ibid.*, 1897, **30**, 28.

B_4. Hypersthene Gabbro near Ambouthra, from *Washington's Chemical Analyses of Igneous Rocks*, 1917, p. 476.

B_5. Dark Basic charnockite, Biligirirangan Hill, Analyst: Chemist M. G. D., *Bull.* **18**, *M. G. D.*, 1945, p. 100.

In the microsection, it is seen to be composed of plagioclase, pyroxene of both rhombic and monoclinic varieties, opaque minerals and a few needles of apatite. The monoclinic pyroxene shows a variation in the optic axial angle (2V) parallel to (010) from 58° to 62°. The plagioclase is polysynthetically twinned, the lamellæ being generally very long and broad. There is neither free quartz nor alkali feldspar.

The mode of the rock determined by actual measurements on the microsection is given below (figures per cent.):—

Plagioclase	58·5
Rhombic pyroxene	30·7
Monoclinic pyroxene	6·1
Ores	4·2
Apatite	0·9

The chemical analysis of this rock along with a few comparable analyses is given in Table IV.

The Basis Composition of type B is as follows:

Kp	1·67
Ne	12·68
Cal	22·36
Cs	2·17
Fo	14·58
Fa	11·18
Fs	2·17
Q	32·04
Ru	0·55
Cp	0·55

The calculated Kata-Norm and C.I.P.W. Norm are shown in Table V.

The two norms agree well with each other as also with the mode; only in the kata-norm does olivine figure out to a minor extent and this can be easily explained as being due to the fact that hypersthene contains normative quartz. According to Winchell (1927), labradorite is capable of taking up into its constitution as much as six per cent. of orthoclase, and accordingly the orthoclase of the norms is surmised to be in solid solution with the plagioclase. The normative plagioclase has an anorthite content of 63, this value being in close accord with the one determined on the Universal stage and deduced from the Niggli diagram, Fig. 1.

Hornblende-hypersthene granulite.—A slightly foliated rock taken from the contact of a norite intrusion in garnetiferous mica-schist (Khondalite), when examined under the microscope exhibited certain peculiar features.

TABLE V

	Kata-Norm	C.I.P.W. Norm
Or ..	2·79	2·78
Ab ..	21·14	19·91
An ..	37·27	37·25
Di ..	..	3·01 1·60 1·32
Hy ..	18·72 12·96	15·90 13·33
Wo ..	1·79	..
Fo ..	0·54	..
Fa ..	0·37	..
Mt ..	2·17	3·01
Il ..	..	1·52
Ti ..	1·65	..
Ap ..	0·60	0·67
H_2O ..	..	0·11
	100·00	100·41

The typical granulitic texture of the norite has given place to a rather faint gneissic texture. A little more than half of the dark minerals consist of laths and prisms of yellow green hornblende with considerable elongation in the direction of foliation, formed as marginal fringes of the granular pleochroic hypersthene. The slide (k/24) also contains grains and coarse plates of green augite reverting to hornblende. The leucocratic base consists of laths of basic labradorite, with bent twin lamellæ, and exhibiting undulose extinction. The amphibolisation of the pyroxenes here has perhaps to be attributed to an influx of alumina from the para-schist.

Basic Garnetiferous Norite.—A microsection of this rock exhibits intense granulation and some interesting reaction phenomena and throws light on the origin of garnet.

The reaction border always appears where the garnet meets the pyroxene or its alteration product—hornblende. The one conspicuous feature about the reaction rim between pyroxene and garnet is that there is hornblende always formed in between the two minerals. Thus the amphibolisation of the pyroxene seems to be a prelude to its final transformation into garnet. The incipient serpentinization of the pyroxene is also to be seen. The plagioclase exhibits strain effects, like undulose extinction and bent twin lamellæ.

Ghosh (1941) has set down the various reactions by which garnet appears to have been developed. Groves (1933) explains the origin of garnet by the following formulæ:

Diopside + Anorthite = Garnet + Quartz.

In view of the undoubted rhombic nature of the pyroxene and its ultimate transformation into garnet, the following sequence of changes is suggested to have taken place:

Hypersthene – Hornblende + Plagioclase = Garnet + Quartz.

C. *Intermediate Charnockite* (*Normal Quartz Dioritish* ?).—It is dark grey in colour and consists essentially of quartz, felspar and pyroxene. Its specific gravity varies between 2.71 and 2.80.

TABLE VI

Analyses of Intermediate Charnockites

	C	C_1	C_2	C_3	C_4	C_5
SiO_2 ..	59·29	69·60	69·10	69·44	62·85	61·80
Al_2O_3 ..	14·22	12·10	11·69	12·90	14·87	16·26
Fe_2O_3 .	1·21	0·58	2·63	2·93	2·32	1·75
FeO ..	5·18	6·30	3·38	3·83	5·07	6·04
MnO ..	0·92	0·23	0·04	0·26	0·05	0·07
MgO ..	1·88	2·27	1·26	1·74	3·29	3·56
CaO ..	2·75	4·58	2·62	3·48	4·48	4·30
Na_2O ..	4·01	0·88	3·59	4·05	3·72	3·40
K_2O ..	0·98	0·92	4·55	0·54	1·09	1·16
TiO_2 ..	0·62	1·38	1·23	0·80	0·83	0·32
P_2O_5 ..	..	0·28	0·05	0·12	0·08	0·08
H_2O ..	0·40	0·72	0·28	0·42	0·11	0·26
H_2O ..	0·05	0·07	0·16	0·20		0·65
Others ..	..	..	0·13	..	0·19	0·54
Total ..	101·51	99·91	100·71	100·71	98·95	100·19
			Niggli values			
si ..	290·5	309·0	291·0	293·7	223·0	206·4
al ..	35·0	31·0	36·0	32·0	30·6	31·9
fm ..	33·5	41·0	33·0	31·2	37·7	39·3
c ..	12·5	22·0	11·0	15·7	14·9	15·4
alk ..	19·0	6·0	20·0	18·1	17·8	13·4
ti ..	2·0	4·4	4·5	2·5	2·1	0·8
k ..	0·13	0·42	0·12	0·08	0·15	0·18
mg ..	0·37	0·37	0·38	0·32	0·46	0·45

C. Intermediate charnockite from the main range of hills in Kondapalle, west of ·245, Analyst: M. Sriramarao.

C_1. Hypersthene granulite, Alma Beach, Alfred Country, Natal, Analyst: J. C. Dunne, *Trans. Geol. Soc. S. Africa*, 1943, **45**, 201.

C_2. Charnockite one mile from Hapatula, Ceylon, 300 ft. from the surface of intrusion, Analyst: R. J. C. Fabry, *Canad. Jour. Res.*, 1929, **1**, 481.

C_3. Darker layer in the acid charnockite, Biligirirangan Hill, S. E. Mysore, Analyst: H. V. Krishnayya (1919).

C_4. Intermediate charnockite—Quartz hypersthene diorite from Yercaud, Shevaroy Hills, Madras, Analyst: H. S. Washington (1916).

C_5. Quartz hypersthene diorite: Bunvore district, Uganda, Analyst: A. W. Groves, *Q. J. G. S.*, 1935, p. 166.

Under the microscope, quartz with minute opaque dusty inclusions is abundant and it is difficult to distinguish these rocks from the still more acid members. The alkali felspar is all microcline-micro-perthite and the plagioclase corresponds in composition to oligoclase or acid andesine. The pyroxene is hypersthene but for some occasional augite. There is the accessory —titaniferous magnetite.

The abundance of plagioclase is myrmekitic intergrowth with quartz definitely relegates this member to the intermediate division. Mortar structures, bent twin lamellæ and brush polarisation—all point to the rock having been subjected to stress. The parallel arrangement of the mafic and felsic minerals is perhaps the effect of such stress.

The mode of the rock is given below (figures per cent.):—

Quartz	25·5
Alkali felspar (Microcline-micro-perthite)	18·1
Plagioclase	38·2
Hypersthene	12·5
Augite	1·4
Ores	2·8

In Table VI, column C, is given the chemical composition of the rock. For purposes of comparison, analyses of intermediate charnockites from other localities are given.

The basis of type C is as follows:—

Kp	3·38
Ne	21·97
Cal	8·29
Sp	2·70
Fo	2·70
Fa	6·08
Fs	1·18
Q	53·27
Ru	0·40

The kata-norm and C.I.P.W. Norm of the same rock type are arranged in Table VII.

TABLE VII

	Kata-norm	C.I.P.W. norm
Or ..	.. 5.63	5.56
Ab ..	.. 36·62	34·06
An ..	.. 13·82	13·62
C ..	.. ..	1·63
Cord ..	.. 4·95	..
	3·60	4·70
Hy ..	.. 7·32	7·52
Mt ..	.. 1·18	1·62
Il ..	.. ..	1·22
Ru ..	.. 0·45	..
Q ..	.. 26·45	30·12
H_2O ..	.. ..	0·45
	100·02	100·50

A glance at the above table shows that the corundum and excess quartz of C.I.P.W. Norm appear as cordierite in the latter. A comparison of the norm and mode shows that normative orthoclase appears as perthite in the mode. The plagioclase as calculated from the norm, has a composition approximating to 32 per cent. anorthite, this value corresponding closely with the Federov Stage determinations and deductions from Niggli's diagram. The corundum and cordierite of the norms might have been taken up by the modal hypersthene.

The Niggli values of the Intermediate charnockite do not exactly fit into any one of the magma types of Niggli. They show only a close approximation to his quartz-dioritisch magma. A possible explanation for this feature is offered in the section under petrogenesis.

D. *Acid Charnockite* (*Engadinitgranitisch*).—This rock type as seen in hand specimen, shows little difference from the preceding variety. It consists of the same blue quartz, felspar, pyroxene and other constituents, but has slightly low specific gravity ranging from 2·60 to 2·69.

Under the microscope, quartz occurs mostly as clusters of rounded blebs in felspar. Myrmekitic and perthitic intergrowths, are common. Hypersthene with its characteristic pleochroism from pale pink to green and with Z to C ang e varying up to 33° was observed. Biotite in red brown flakes and plates rarely figures out prominently, and if it does, it is only at the expense of the hypersthene. A little plagioclase—mostly untwinned—

TABLE VIII

Analyses of Acid Charnockites

	D	D_1	D_2	D_3	D_4	D_5	D_6
SiO_2 ..	73·82	77·47	76·16	71·74	70·63	73·40	69·57
Al_2O_3 ..	14·03	11·00	13·49	11·13	14·34	14·30	15·08
Fe_2O_3 ..	0·05	1·04	0·85	2·96	0·32	1·05	0·26
FeO ..	1·08	2·02	1·67	1·70	2·20	0·78	3·29
MnO ..	0·10	..	0·03	0·53	0·04	..	0·02
MgO ..	1·01	0·43	1·08	0·55	0·56	0·04	2·09
CaO ..	0·91	1·02	1·20	3·42	2·04	1·54	2·62
Na_2O ..	4·05	2·86	2·42	4·65	3·02	6·66	2·87
K_2O ..	3·97	4·14	3·06	2·15	5·59	1·45	3·99
H_2O ..	0·26	0·20	0·80	0·61	0·40	0·04	0·53
H_2O ..	0·09	0·05	..	0·05	0·09	0·16	
TiO_2 ..	0·38	0·26	0·16	0·30	0·61	0·62	0·02
P_2O_5 ..	Nil	..	*n.d.*	0·19	0·25	..	0·04
Others ..	..	..	..	0·05	..	..	0·28
Total ..	99·75	100·49	100·92	100·03	100·09	100·04	100·66
			Niggli values				
si ..	398·0	480·0	455·8	341·0	353·0	385·0	300·0
al ..	44·5	42·0	46·3	31·0	42·0	44·0	39·0
fm ..	16·0	19·5	21·0	24·0	14·5	8·0	26·0
c ..	5·0	7·0	7·4	17·0	11·0	9·0	12·0
alk ..	34·5	30·0	25·3	28·0	32·5	39·0	23·0
ti ..	1·6	1·1	0·7	1·0	2·1	2·4	..
k ..	0·39	0·38	0·44	0·23	0·55	0·13	0·48
mg ..	0·51	0·47	0·45	0·17	0·29	0·04	0·51

D. Acid charnockite from the hill mass close to mile 11/7 on the forest road, Kondapalle, Analyst: M. Sriramarao.

D_1. Charnockite, St. Thomas Mt., Madras, Analyst: H. S. Washington, *Amer. Jour. Sci.*, 1916, p. 325.

D_2. Medium grained greasy looking dark greenish grey acid charnockite near Punajur, Analyst: B. S. Raju, Bull. **18**, *M.G.D.*, 1945, p. 98.

D_3. Charnockite, 3 miles S. E. of Pussellawa, mile post 26 Ceylon, Analyst: E. G. Radley, *Canad. Jour. Res.*, **1**, 1929, p. 482.

D_4. Charnockite, Ivy point, Alfred Country, Natal, Analyst: J. C. Dunne, *Trans. Geol. Soc. S. Africa*, 1943, **45**.

D_5. Charnockite from the hill mass one mile east of Potrelu, Malakanagiri, India, *Rec. G.S.I.*, 1938, 73, 420.

D_6. Acid charnockite between Waki camp and Bukumi camp, Bunyoro District, Uganda, Analyst: A. W. Groves, *Q.J.G.S.*, 1935, **91**, 163.

is observed and determinations on Federov stage on twinned grains show it to be Oligoclase.

The mode of the rock determined micrometrically is as follows:

Alkali felspar (perthitic)	46·9%
Quartz	29·8%
Plagioclase	16·4%
Hypersthene	5·4%
Ores	1·5%

The results of the chemical analysis of this rock are recorded along with those of other comparable ones in Table VIII.

The basis composition of the acid charnockite is shown below:—

Kp	14·16
Ne	21·91
Cal	2·70
Sp	2·36
Fo	0·95
Fa	1·35
Q	56·29
Ru	0·28

The kata-norm and C.I.P.W. norm of the same rock are arranged in Table IX.

TABLE IX

	Kata-norm	C.I.P.W.norm
Or ..	23·62	23·35
Ab ..	36·52	34·06
An ..	4·50	4·45
C ..	..	1·43
Cord ..	4·33	..
..	1·27	2·50
Hy ..	1·80	2·51
Il ..	..	0·76
Ru ..	0·28	..
Q ..	27·68	30·72
H_2O ..	..	0·35
	100·00	100·13

From the table it will be seen that there is a rather low percentage of quartz in the Kata-norm and this can be attributed to the formation of the cordierite from quartz, hypersthene and corundum of the C.I.P.W. norm. A comparison of these with the mode shows that much of the albite of the norms has been used up for the formation of perthite.

GENERAL REVIEW OF THE CHEMICAL COMPOSITION OF THE CHARNOCKITES

From a study of the preceding chemical data it is observed that the charnockites in this area vary from the acid, through intermediate, to basic

and ultrabasic types. Chemically, this expresses itself in the relative proportions of the different oxides. The SiO_2 percentage is from 74 to 50. Alumina is low and it is generally just enough to satisfy the combined alkalies and lime, though in all the members except the norite we see in the C.I.P.W. norm about 1·5 per cent. of corundum. This excess has been accounted for by the aluminous nature of hypersthene. Iron oxides are usually high; hence, the richness in the femic constituents. FeO greatly predominates over Fe_2O_3. Except in type A, MgO is low and considerably below the iron oxides reckoned as FeO. Lime is also not high and in the basic members a part of it goes into the diopsidic molecule to appear as modal augite or hornblende. The alkalies are rather high and it is the Na_2O that always predominates over the K_2O, except in type D where they are nearly in equal proportions. Titanium and manganese are very low, the former showing a progressive increase in amount in the more and more basic members. Phosphorus is present in the basic members and chromium in the ultrabasic ones.

Attention may be drawn to the fact that whereas the gradation between the acid and intermediate varieties is very gradual, the same is not the case between the intermediate and basic varieties. Again, the chemical transition between the basic and ultrabasic types is very gradual. These analytical results are of significance in consideration of the genesis of this rock suite.

E. *Pink Banded Granite Gneiss* (*Yosemitgranitisch*).—Megascopically, it is a compact, medium to fine-grained rock characterised by light and dark coloured minerals. It is highly crumpled and foliated, the gneissic structure being quite evident.

Under the microscope, again, the parallel disposition of the minerals is a conspicuous feature. The principal constituents of the rock are quartz, orthoclase, microcline, plagioclase and biotite. The potash felspar is generally fresh and is dominantly orthoclase. Quartz occurs as long lenticles and a rough parallelism to 'augen' structure is exhibited. Where this structure is developed, the 'augen' structure is made up of quartz, in rare cases, of felspar. The salic minerals all exhibit strain effects like undulose extinction and intense peripheral granulation. The plagioclase, as determined by Universal stage measurements, is oligoclase with 15 per cent. anorthite. The biotite is a dark green variety, quite distinct from the common red brown variety of aluminous schists. It is very feebly pleochroic. Zoisite and magnetite occur as accessory minerals.

The results of the micrometric analysis of the rock are as follows:—

Quartz	34·0%
Alkali felspar	35·1%
Plagioclase	22·9%
Biotite	7·0%
Accessories	1·0%

The chemical composition of the rock is given in column E of Table X, the remaining columns in the table containing the values for comparable types.

TABLE X

Analyses of Pink Banded Granite Gneiss and Related Rocks

	E	E_1	E_2	E_3	E_4
SiO_2 ..	74·28	71·40	75·50	71·40	73·33
Al_2O_3 ..	13·04	14·31	13·92	13·50	14·78
Fe_2O_3 ..	0·55	1·02	0·48	1·10	0·46
FeO ..	2·07	1·94	1·17	2·83	0·84
MnO ..	..	0·06	..	0·03	0·10
MgO ..	0·81	0·30	0·52	0·55	0·40
CaO ..	1·38	2·11	3·54	1·72	1·72
Na_2O ..	2·93	3·52	3·64	4·02	3·94
K_2O ..	4·62	3·64	0·74	2·88	4·89
TiO_2 ..	0·12	0·32	0·08	0·58	..
P_2O_5 ..	..	0·27	..	..	0·04
H_2O ..	0·57	0·46	0·15	..	..
BaO ..	..	0·06	..	..	..
CO_2 ..	..	..	..	0·68	..
Total ..	100·37	99·41	99·94	99·29	100·50
		Niggli values			
si ..	402·0	370·0	420·0	366·1	383·0
al ..	42·0	43·5	46·0	40·6	45·5
fm ..	19·0	15·0	11·0	20·9	8·8
c ..	8·0	11·5	21·0	9·2	9·7
alk ..	31·0	30·0	22·0	29·3	36·0
ti ..	0·5	1·2	0·3	2·1	..
k ..	0·51	0·40	0·12	0·32	0·45
mg ..	0·34	0·25	0·41	0·21	0·36

E. Pink banded granite gneiss from the main range of hills, one mile north of Kondapalle, Analyst: M. Sriramarao.

E_1. Coarse granite gneiss, N. W. of Siljadih, Analyst: L. A. N. Iyer, *Rec. G. S. I.*, 74, 502.

E_2. Enderbite, Proclamation Island, Enderby Land, Antarctica, Analyst: C. E. Tilley, *Geol. Mag.*, 1936, 73, 314.

E_3. Closepet granite (fine pink granite) Analyst: Chemist, M.G.D., 1940, *M.G.D. Bull.*, 17, 94.

E_4. Peninsular Gneiss (Light grey fine-grained gneiss), Analyst: Chemist, M.G.D., *Bull.*, 1940, 17, 94.

The basis composition of the type E is as follows:—

Kp	..	16·60
Ne	..	15·92
Cal	..	4·23
Sp	..	1·18
Fo	..	1·12
Fa	..	2·80
Fs	..	0·50
Q	..	57·54

The Kata-Norm and C.I.P.W. Norm are shown in Table XI.

TABLE XI

	Kata-norm	C.I.P.W.norm
Or ..	27·66	27·24
Ab ..	26·53	24·63
An ..	7·05	6·95
C ..	..	0·71
Cord ..	1·89	..
Hy ..	1·59	2·00
..	3·40	3·82
Mt ..	0·50	0·70
Il ..	..	0·15
Q ..	31·38	33·78
H_2O ..	..	0·70
	100·00	100·68

A comparative study of the norms and mode brings out their close correspondence, except for the fact that the whole of corundum and hypersthene of the C.I.P.W. Norm and the cordierite and hypersthene of the Kata-Norm go into the constitution of the complex silicate—mica. The modal alkali feldspar is slightly greater in amount and this is due to its ability to take up as much as one-fourth of its amount of albite in solid solution.

PETROCHEMISTRY

The chemical analyses of the four types of charnockites expressed as weight percentages of the chief oxides are not by themselves suitable for petrographic classification and comparison or for understanding their evolution. For such a study various new values have to be calculated by grouping together allied oxides, having the molecular proportions of the various oxides as the basis of calculations according to the method of Niggli which is very helpful in the study of differentiation and magmatic affinities of rocks.

Trends of Differentiation in Charnockites.—The rock types studied show a wide range of variation in the silica content—from 50 to 74 per cent. This, together with the variation in the Niggli values, as for example, *si* from 398 to 87, goes to show that the magma from which these types were formed did undergo extensive differentiation. One feature worthy of note is that there is a well marked gap between *si* 290 and 117, which is of great significance in the nature and evolution of these rocks.

Fig. 3 represents a generalised differentiation diagram drawn from the Niggli values, with *si* as abscissa and the other constituents as ordinates. There are two sets of sympathetic curves—the *c*, *fm* and the *al*, *alk* curves—and each set is again mutually antipathic to the other. The *c* curve which initially has a steep rise from 6 to 24 in a *si* range of 87 and 124, later, falls gently reaching a minimum of 5 at *si* 400. The *fm* curve which is sympathetic to it slopes down abruptly in the beginning and gradually later. The *al* and *alk* curves rise gently. The Isofalic point, *i.e.*, the point of intersection of the *al* and *fm* curves is at a *si* value 248.

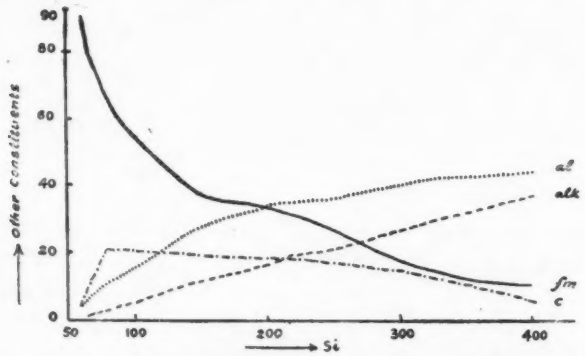

FIG. 3. Differentiation diagram of the charnockite series.

In Fig. 4 is shown for comparison the differentiation diagram of calc-alkali series constructed by Niggli. It will be seen that there is a marked similarity between the two diagrams. This feature points to the strong affinity of the charnockites to the rocks of the Circum-pacific suite. This fact receives further confirmation from the observation that the Isofalic point falls at a *si* value of over 160, as in all other rocks belonging to this suite.

That the charnockites belong to the Circumpacific suite is also evident from a study of the *k-mg* diagram (Fig. 5), wherein *k* represents the amount of potash in the total alkalies and *mg* the amount of magnesia in the total

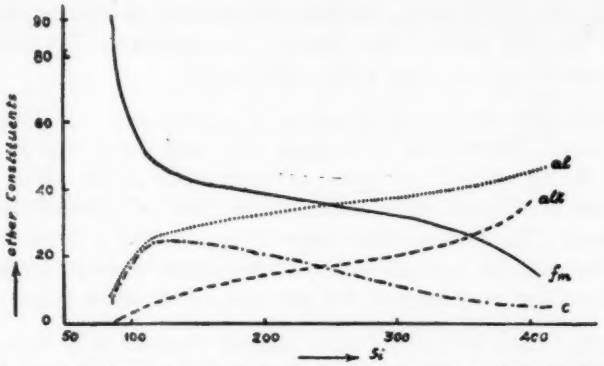

FIG. 4. Differentiation diagram of the Calc-alkali Series (after Niggli).

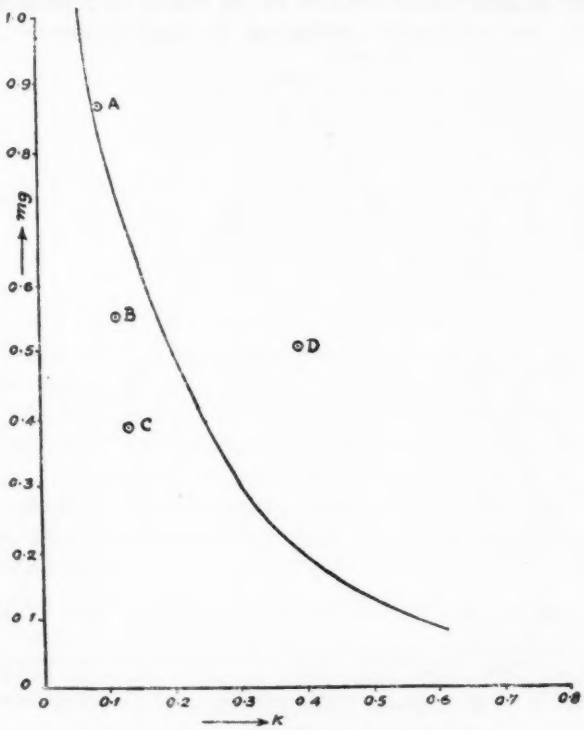

FIG. 5. *k-mg* Diagram of the charnockites.

ferro-magnesian constituents. During the progress of differentiation there should be a reciprocal relationship between the two values in the case of

rocks of the Calc-alkali suite. In fact, this sort of relationship is exhibited here by all the rock types except the acid charnockites. The cause of this anomaly is explained in a later part of this paper.

The normative mineral composition of a rock can be estimated from its Niggli values. When there is enough silica and when *al* is less than the sum (*alk*+ *c*), the value 2 *alk* gives the proportion of the alkali feldspars, 2 (*al-alk*) that of the anorthite content and (100-2 *al*) that of the melanocratic minerals. The sum of these three values is always equal to 100 and can be represented by a single point in a trilinear co-ordinate diagram in which the three corners represent 100 per cent. of the three values.

When the values are plotted on a trilinear diagram (Fig. 6) a clear idea is gained of the basicity of the rocks and also of the general trend of consolidation of the magma which conform to the theory of crystallization-differentiation, *viz.*, the progressive enrichment in alkali feldspar.

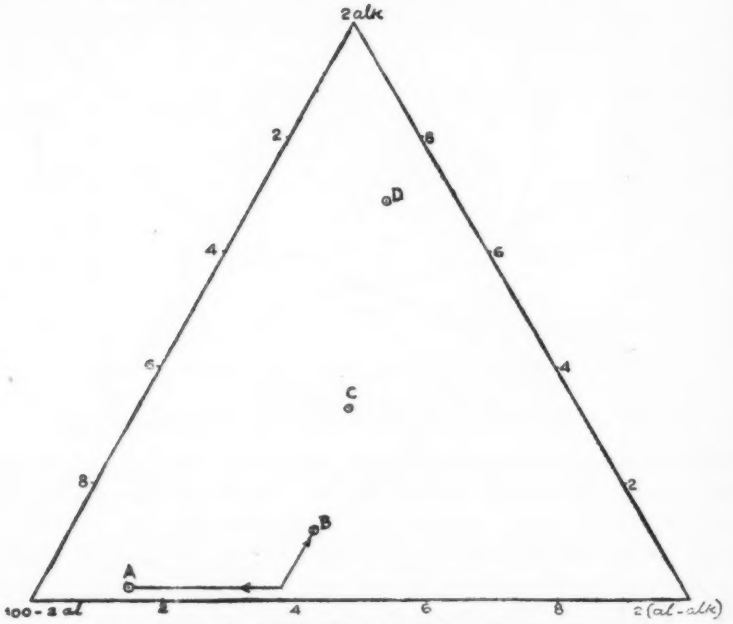

FIG. 6. 2 *alk*, 2 (*al-alk*), (100–2 *al*) diagram for the Charnockites.

The general sequence is that from a common parent magma there are three different lines of development during the evolution of the various rock types.

(1) The impoverishment in ferromagnesians with constant alkali feldspars,

(2) The enrichment in alkali feldspars with constant dark minerals,

(3) The enrichment in alkali-feldspars with constant anorthite content.

From the point B the last trend operated and resulted in type C. From this, again, by the same process is derived type D, though there is a slight decrease of anorthite from type B to D.

The Q.L.M. Diagram

The Q.L.M. and π, γ values of the charnockites are shown in Table XII.

Table XII

Q.L.M. and π, ν Values of the Charnockites

	A	B	C	D
Q ..	22·2	32·0	53·2	55·8
L ..	12·0	36·7	33·6	38·6
M ..	65·8	31·3	13·2	5·6
π ..	0·71	0·61	0·25	0·07
γ ..	..	0·07	..	..

When the Q.L.M. values (Table XII) of the charnockites are plotted in the diagram (Fig. 7) prepared by Niggli (1938, Figs. 2 *a*, 20 and 21), it is seen that only the point B falls below the line PF (Saturation line) and above the line PL in the region of 'Normal Basalt'. The rest fall outside this region. All primary magmas are confined to the composition limited by the region of 'Normal Basalt' and as norite (B) falls within the borders of the above-mentioned field, it is the parent magma for the Kondapalle charnockites.

The most striking feature about the differentiation diagram of the charnockites is its very close resemblance to that of the Bushveld Igneous Complex. For the sake of comparison, the latter constructed by Niggli (1938, Fig. 20) is shown in Fig. 8.

In both cases the parent magma is the same, *viz.*, norite. From the figure it is further evident that the dotted line encloses the field of the Circum-pacific (calc-alkali) suite of rocks. Though there are four possible trends

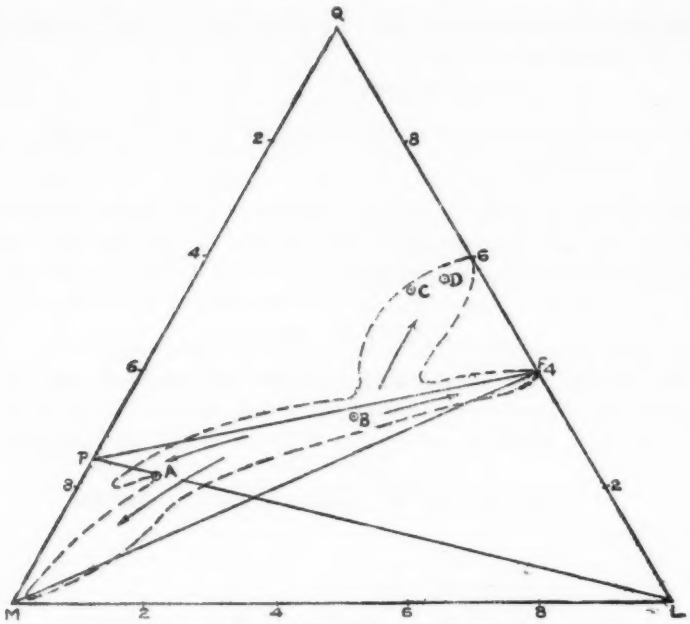

FIG. 7. Q L M diagram for the Charnockites.

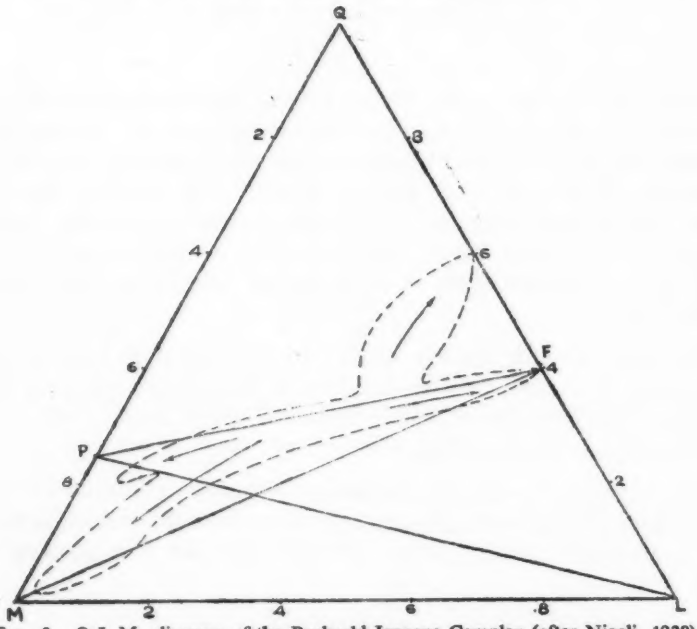

FIG. 8. Q L M diagram of the Bushveld Igneous Complex (after Niggli, 1938).

of differentiation only two—the second and fourth—are represented:

(1) Norite to anorthosite .. .. **BE**
(2) Norite to pyroxenite .. .. **BP**
(3) Norite to peridotite .. .. **BM**
(4) Norite to granite .. .. **BQ**

by the charnockites of Kondapalle.

The remarkable similarity between the two regions—Bushveld and Kondapalle—can further be appreciated from the following facts:—

(i) the same parent magma and the same basic rocks—norite,

(ii) the ultrabasic differentiates—bronzitites—are common,

(iii) the results of residual magma differentiation—the granophyres and granites of Bushveld—compare favourably well with the intermediate and acid charnockites,

(iv) consequential similarities in variation diagrams, differentiation diagrams, etc.,

(v) ' the transitional manner by which the various types are connected' pertains to both areas,

(vi) lastly, the occurrence of chromite and its association with the basic and ultrabasic rocks in the two regions.

The k, π and mg γ Diagrams.—The trends of differentiation in charnockites detailed above are also made evident by a study of the interrelation between the three Basis molecules *Kp*, *Ne* and *Cal* which is brought about by *k* and *π* values themselves on a triangular diagram whose corners are *Kp*, *Ne* and *Cal*, in which the three generalised diagrams constructed by Niggli (1938, Figs. 2*b*, 3*b* and 4*b*) for the three petrographic suites are included in a simplified form. When the *k* and *π* values for the charnockites are plotted in the diagram (Fig. 9) it is seen that all the types except type C fall within and close to the boundary of the pacific suite. Even type C falls only slightly outside the boundary, the reasons for this anomaly being explained in the section ' petrogenesis '.

Similar indications of the Pacific trend of differentiation are obtained from a study of *mg γ* diagram which represents the interrelation of the four basis molecules Fo, Fa and Cs expressed as three values Mg, Fe and Ca. In Fig. 10 in which the three generalised diagrams constructed by Niggli (1938) for the three suites are included, when the values for type B are plotted, the projection point falls well within the region of the Pacific suite.

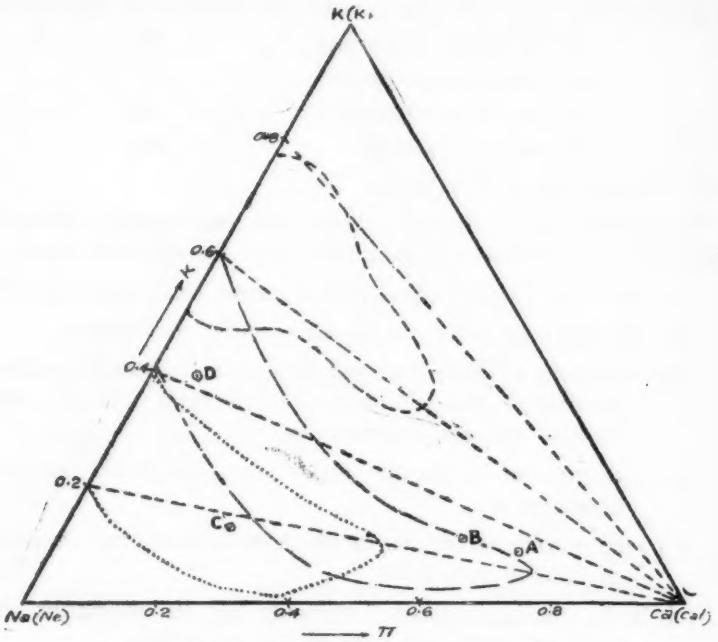

FIG. 9. $k\,\pi$ diagram for the Charnockites.

Pacific
Mediterranean
Atlantic

It is apparent from the above discussion that the charnockites of this area are the differentiation products of a basic igneous magma and that they show unmistakable affinities to the Circumpacific suite of rocks.

PETROGENESIS

There is diversity in the opinion on the origin of charnockites (Rama Rao, 1945).

So far as the charnockites of the Kondapalle hills are concerned, we have to note the following:

There is a gradation from the acid through intermediate to basic and ultrabasic types, and this is explained as being presumably due to differentiation of a basic parent magma.

There is a slight difference in the composition of hypersthene from one rock type to the other. For example in the pyroxenite, the pyroxene is really

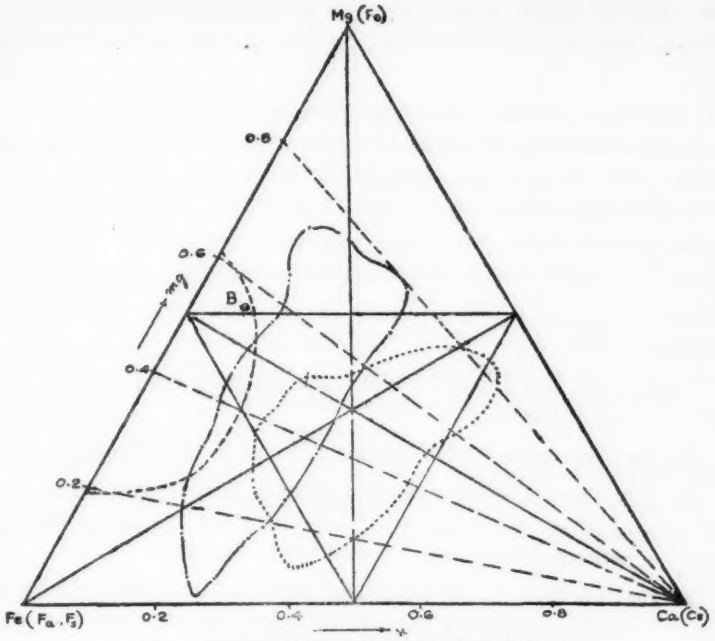

FIG. 10. *mg r* diagram for the Charnockites.

Pacific
Atlantic
Mediterranean

bronzite, while, in the other types it is hypersthene; thus, definitely pointing to a noticeable increase in the FeO/MgO ratio. This is in accord with the trend of crystallization in mafic magmas.

It is, however, recognized here that there has been a certain amount of assimilation of argillaceous material by the magma, giving rise to the aluminous hypersthene. This is in conformity with the observations of Crookshank (1938) from a study of the charnockites of the Eastern Ghats. Again, the complete amphibolization of the pyroxene in the charnockites at the contact of the khondalite members supports this view.

The wide gap in the *si* value from 290 to 117 is indicative of the absence of rocks intermediate in composition between norite and intermediate charnockite and points to some extraneous source which considerably has affected the *si* value of the latter. It is perhaps by virtue of this incorporation of foreign material that on analysis the Niggli values of the rock type

C are observed not to fit into any one of the magma types of Niggli. Its anomalous position in the K, π diagram has also perhaps to be ascribed to this.

It is therefore surmised that there is a widespread granitization of these acid and intermediate differentiates by the intrusive granite together with complete reconstitution and recrystallization. This is perhaps the cause for the discrepancy exhibited by type D in the *k-mg* diagram (Fig. 5).

The granites and charnockites are later subjected to lateral earth movements resulting in banding and rough gneissic structure.

From a field and laboratory study of the rocks of this region, the author concludes

(i) that the charnockites are the differentiation products of an original basic magma,

(ii) that the magma has assimilated some of the khondalitic material,

(iii) that the associated younger granites have reacted with the charnockites resulting in the obliteration of gradational types between the intermediate and basic members,

(iv) that all these rocks were later subjected to compressional movements which have resulted in impressing on them such features as banding, tendency towards gneissosity, crumpling and folding and minor stress effects such as granulation, brecciation, undulose extinction, brush polarisation, etc.

Chromite

The unique association of chromite with charnockites reported by M. S. Krishnan (1944) gave prominence to Kondapalle.

Mode of occurrence and association.—In an area of about 8 × 5 miles in the Eastern part of the hills, there are two big quarries and a dozen small excavations, which gave an opportunity to study its mode of occurrence and genesis. The series occur (1) as irregular views in the country rock with variation to minor bands or ribbon-like bodies in the rock and (2) as definite lenticular and pocket-like bodies. The former is most common and the latter is found in a quarry near the mile 2/4 on the forest road. Some of the lenses have a thickness of 4 to 5 ft. and have sharp boundaries with the country rock. Like all other Indian occurrences except Singhbhum, chromite of Kondapalle is associated with magnesite (big quarry) which occurs in thin stringers in serpentenised schists and talc schists. In Singhbhum chert (Mahadevan, 1929) occurs in association.

Nature and Composition of the Ore.—There are two types of ore—hard ore and soft ore—corresponding to the hard and soft varieties of the ore-bearing pyroxenites.

Hard Ore.—This is generally black, well-cemented, massive and denser than the soft ore. It occurs mostly as lenses and pockets in the pyroxenites.

Scattered on the outcrops of the ore bodies and also in the nalas is found a type of ore which has a pitted appearance and a dark brownish surface tint. The pittedness is perhaps due to the solvent action of water and the brownish tint to limonitic coating. Such a type of ore is familiarly known as ' Top Ore '.

Soft Ore.—This is an intermixture of the highly serpentinized pyroxene with chromite. The action of percolating waters seems to have made the ore soft and porous. It can be easily crushed and is sometimes soft enough to be disintegrated by the fingers.

The percentage of chromic oxide in the above-mentioned types of ore are determined. The results are shown in Table XIII along with those of other analyses of chromites from the same area, quoted from Krishnan's paper (1944).

TABLE XIII

Analyses of Chromite of Kondapalle

	A	B	C	D	E	F	G	H
Cr_2O_3 ..	43·07	40·54	50·67	46·16	38·89	55·6	42·6	49·5
FeO ..				23·06	22·75	20·0	19·8	19·5
SiO_2 ..				0·68	6·32	8·8	.	..
Al_2O_3 ..				17·9	17·35	7·8	..	..
CaO ..				2·65	2·66	0·2	..	..
MgO ..				9·2	10·21	12·2	..	..

A. Hard Ore
B. Soft Ore
C. Top Ore
} Analyst: M. Sriramarao.

D. Lump of detrital chromite
E. Hard fresh chromite
} Analyst: G. S. I. Laboratory.

F. High grade detrital ore
G. Soft Ore
H. Typical concentrate from soft ore
} Analysis kindly supplied by the Rajendra Mining Syndicate.

From the table it will be seen that the percentage of Cr_2O_3 is maximum in the Top ore and minimum in the Soft ore.

Chromite, as observed in thin section, has a uniform black colour. It exhibits considerable variation in its degree of crystallization. The grains

from hard ore are euhedral, and those from soft ore are subhedral, the latter form being indicative of the action of corrosive solutions.

Genesis of the Ore.—There is a good deal of controversy about the origin of chromite. (Fermor, 1919; Sampson, 1929; Ross, 1929; Fisher, 1929.)

The author believes that though some of the chromite of Kondapalle might have crystallized at an early magmatic stage, most of it has been formed in the late magmatic and hydrothermal stages as in the Ratnagiri and Singhbum deposits studied respectively by L. A. N. Iyer (1939) and Bhadauria (1943) respectively.

The field and laboratory evidence in support of the said view are set down below:

Field Observations.—Veins of chromite cutting the serpentinized pyroxenite; definite association with the hydrothermal mineral-magnesite.

Microscopic evidence.—The subhedral nature of many of the chromite grains; typical mineral assemblages—chlorite and serpentine—of the hydrothermal processes; and deposition of chromite along the contact planes of the different pyroxene crystals in pyroxenites.

It is therefore suggested that the first mineral to crystallize out from the magma was the pyroxene. The chromite began to crystallize then and it occupied the interstitial spaces. During and just after this stage, the rock was subjected to deuteric changes whereby the pyroxene was serpentinized. The serpentinization was brought about by waters charged with CO_2, as evidenced by the occurrence of magnesite. There is evidence of both solution and redeposition of chromite by these hydrothermal processes which are again the cause for the local development of talc-schists.

Summary and Conclusion

The results of a detailed field and laboratory study of the different types of charnockites, the granite gneiss and the ore mineral—chromite—are given. Four types of charnockites, representing the acid, intermediate, basic and ultrabasic divisions, were chemically analysed and the analyses interpreted after the manner of Niggli. Their petrographic descriptions together with those of other related ones are also given. It was proved beyond doubt that the charnockites are of igneous origin and that though they exhibit differentiation relationship to one another, yet in view of some anomalies the importance of possible assimilation in their gnesis is alluded to.

The occurrence of chromite in the basic and ultrabasic members of charnockite series is described, the results of the analyses of the ore presented and hydrothermal origin proposed.

Acknowledgments

The author is greatly indebted to Professor C. Mahadevan for much helpful and constructive criticism and for facilities for work in the laboratories of the Andhra University and to Dr. M. S. Krishnan for valuable suggestions and for facilities for consulting the necessary literature. He is thankful to Dr. K. P. Rode for suggesting the problem and to Mr. C. Karunakaran for his keen interest in the work.

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PHYSICO-CHEMICAL STUDIES WITH AQUEOUS FLUORIDE SOLUTIONS

Part II. Hydrogen and Oxygen Overvoltages in Hydrofluoric Acid

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The current-voltage curves for the electrolysis of aqueous solutions of alkali fluorides and ammonium fluoride show two breaks in each case.[6, 14] The first one undoubtedly refers to the primary decomposition of water. Earlier workers[6] regard the second break as a mere duplication of the first break, differing from it only by the inclusion of hydrogen and oxygen overvoltages in the measured potential for the second break. From other considerations, however, the second break appears to be due to a different electrode process than that occurring at the first break.[14] A knowledge of the hydrogen and oxygen overvoltages in hydrofluoric acid solutions at the relevant current densities is necessary to elucidate the point further. No such data are, however, available although hydrogen and oxygen overvoltages and related phenomena have been widely studied in a variety of other solutions and under various conditions.[2, 9, 10] In view of the general importance of overvoltage phenomenon in a study of irreversible electrode processes, it appeared desirable to make a detailed study of hydrogen and oxygen overvoltages in aqueous solutions of hydrofluoric acid.

Experimental

A. R. quality Merck's hydrofluoric acid and Kahlbaum's potassium hydroxide and oxalic acid were used in preparing the solutions. All vessels, etc., required for use with hydrofluoric acid were coated with pure paraffin wax if not entirely made of this material.

For the determination of hydrogen overvoltage, hydrofluoric acid solutions were prepared in redistilled water which had been freed from dissolved oxygen by prolonged boiling and subsequent cooling in a current of hydrogen. The solution was further saturated with hydrogen and kept in a hydrogen atmosphere. All other solutions were prepared in redistilled water only.

Pure potassium hydroxide solution kept in wax-coated vessel to prevent contamination with silica from glass was used as the intermediate titrant in preparing the hydrofluoric acid solutions. During titration the alkali was taken in a glass burette as the time of contact with glass was not sufficiently long for detectable quantities of silica to be dissolved; perfectly sharp end-point was obtained. The fundamental standard in preparing the solutions was oxalic acid, and phenolphthalein served as indicator.

A decinormal calomel half-cell checked against a hydrogen electrode was used as the reference electrode. Hence, to prevent contamination of the electrolyte, electrical connection with the reference electrode was made in a side tube[11] connected with the electrolytic cell which was a round-bottomed beaker of about 400 c.c. capacity. The tip of the side tube projecting inside the cell had only a small opening, slightly less than 1 mm. in diameter[12] and this opening was plugged with a tiny roll of hydrofluoric acid-washed filter paper to prevent bubbles of gas evolved on the test electrode from entering into the tube, and thus breaking electrical connection with the reference electrode.

The cell was provided with a close fitting wooden stopper soaked in paraffin wax which carried a hydrogen inlet tube, a thermometer, and a wax tube stopped at the bottom by means of a tight roll of hydrofluoric acid-washed filter paper. This tube enclosed the other electrode necessary for the passage of electric current through the solution, so that access to the test electrode of the depolarising gases evolved at this other electrode was prevented. This other electrode consisted of platinized platinum to avoid its polarisation during electrolysis.

The test electrode was introduced into the cell through another hole in the stopper which was, when not in use, closed by a tight fitting cork carrying the hydrogen-outlet tube; this was protected from the air by a gas-bubbler.

The test electrode was rotated rapidly during measurement to avoid concentration polarisation, and the rotation was made slightly eccentric so as to prevent the electrolyte from being dragged in rotation. The distance between the rotating electrode and the tip of the side tube which served to make electrical contact between this electrode and the reference electrode, was arranged to be as small as possible (about 1 mm.) in order that any appreciable IR drop may not be included in the potential measurements. The device used for rotating the test electrode was similar in principle to that of Harkins and Adams,[8] but differed from it in constructional details. Different electrodes might be fitted interchangeably to this device, as needed.

The following metals were used as cathode materials:—Pt, Ag, Al in the form of thin wires of about 1 mm. thickness (Kahlbaum A. R. quality); Cu, Au, Ni, Co, Cr, Fe and Zn in the form of thin film electrodeposited on copper wires under such conditions that smooth, adherent, thick coatings were obtained.

Hydrogen required for the work was prepared by electrolysis of 15% potassium hydroxide solution in the usual type of hydrogen generating apparatus of suitable capacity, and passed through alkaline pyrogallol to free it from any traces of oxygen, then through two wash bottles each containing the same solution as the electrolytic cell, for saturating the gas before it entered the latter.

The polarising current was drawn from a number of storage batteries. It was determined by measuring the fall of potential across a suitable standard resistance in the circuit and was read on a sensitive unipivot galvanometer which could be used, by means of suitable shunts, to read small as well as large currents. A potentiometer of the " Land und Seekabelwerke " type in conjunction with a sensitive L & N type galvanometer was used for measuring the required potentials. The Standard Weston cell, used in adjusting the potentiometer for measurement, was checked against one having the Bureau of Standards' Certificate.

For the determination of hydrogen overvoltage the electrolytic cell, kept at $25° \pm 0{\cdot}1°$ C. in an electrically controlled thermostat, was swept out with hydrogen; then with the current of hydrogen still continuing, it was filled with the oxygen-free solution, the side tube and the anode compartment being filled first. During this operation some air got into the cell; this was, however, soon replaced by the current of hydrogen and the bubbling of hydrogen was continued overnight to remove all possible traces of dissolved oxygen before taking readings. Hydrogen was passed continuously during a measurement and between successive measurements also in order to keep the solution always saturated with hydrogen so that any air which might have entered the cell at the time of introducing the cathode is easily swept out before the polarisation potential is measured.

The cathode to be used was polished with the finest grade emery powder on chamois leather, then rubbed clean with wet filter-paper, rinsed thoroughly with redistilled water, wiped dry with clean filter-paper, and attached to the rotating device. The apparent area exposed in each case was $\frac{1}{2}$ sq. cm. The Pt cathode was flamed before being polished and washed, as otherwise difficulty was experienced in obtaining reproducible results with this metal. The cathode was prepared in the method described above

for each determination. In cases where the cathode was affected in such a way that its surface could not be renewed by this treatment, a fresh cathode was used for each determination. This procedure had to be adopted specially in the case of Al.

The current indicating galvanometer was adjusted to read the desired current just before making a determination. This adjustment could be made without polarising the electrolytic cell. The external variable resistances were adjusted to give the required current and the polarising circuit was completed by introducing the cathode into the cell. This method of 'striking' the current with the cathode was followed in order to prevent purely chemical attack, if any, before the electrode is polarised.

The polarisation potential was measured at the end of two minutes. During this time the current was kept constant by adjusting the variable resistances in the circuit. The adjustment of the potentiometer was checked and electrical connection between the reference calomel electrode and the polarised electrode was made just before measuring the polarisation potential.

The procedure of measuring the polarisation potential within a few minutes of starting of the current was followed because, in the first instance, all the metals used except Pt, Ag and Al, were in the form of electrodeposited films on which overvoltage has been shown by Hickling and Salt[9] to attain its maximum value in a few minutes. In the present case this state was generally reached in about two minutes. This was found to be the case with Al also. In the case of Pt and Ag, however, the overvoltage was still increasing after 2 minutes; but, apart from the consideration of preventing the condition of the surface from altering in various ways by continued electrolysis,[5, 6, 15] the procedure of measuring the polarisation potential at the end of two minutes had to be followed in these cases also for the following reason. Due to paraffin wax being a bad conductor of heat, long continued electrolysis caused local heating inside the wax-coated electrolytic cell, and particularly inside the anode chamber which was entirely made of paraffin wax. Even at a c.d. of about 0·1 amp./sq. cm., this local heating became so serious that the wax tube which constituted the anode chamber melted away round about the anode on electrolysing for about 10 minutes only. On this account also readings could not be taken at current densities higher than those used.

After measuring the polarisation potential at any c.d. the cathode was removed from the cell, thus stopping the current, and the polarisation allowed to decay completely before taking the next reading,[9] which was

otherwise found to be affected. Moreover, unless the electrode is initially in virgin condition for each c.d., the readings obtained at different current densities would refer to different initial states of the electrode and electrolyte, and hence would not be comparable. Usually about an hour's rest was sufficient for the decay of polarisation set up at any of the current densities used.

Determinations were usually made starting with the lowest c.d. and ending with the highest c.d. used, taking a number of readings, usually 5 or 6, at each c.d. It was immaterial, however, whether the readings were taken in an ascending or descending or any other order of c.d. if the procedure mentioned above is followed. In fact in those cases where the cathode gets attacked at the lower current densities used, measurements were made in the descending order of current density.

After finishing the series of measurements with one metal, the potential difference between the reference calomel electrode and a hydrogen electrode in the same solution and under similar conditions as used for measuring the polarisation potentials was determined. The difference between the measured polarisation potential at any current density and the potential of the reference calomel electrode as measured against the hydrogen electrode in the same solution is the hydrogen overvoltage at that current density.

Hydrogen overvoltages were thus determined on Pt in N solutions of hydrofluoric, sulphuric, formic and acetic acids, and on Pt, platinized Pt, Ag, Au, Cu, Ni, Co, Cr, Fe, Al and Zn in N/5 hydrofluoric acid solution at $25° \pm 0{\cdot}1°$ C. at current densities ranging from 5×10^{-5} to 1×10^{-1} Amp./sq. cm.

Similarly oxygen overvoltages were determined in an oxygen atmosphere on Pt in N and N/5 solutions of hydrofluoric acid. The oxygen overvoltage at any c.d. is equal to the difference between the anode polarisation potential at that current density measured against calomel electrode and the potential of this calomel electrode against an oxygen electrode in the same solution. Since a perfectly reversible oxygen electrode cannot be realised in practice, its potential has been obtained indirectly as the difference between the theoretically calculated value for the electromotive force of the reversible H_2—O_2 cell, $1{\cdot}23$ volts,[1] and the measured potential difference between the calomel electrode and a hydrogen electrode in a solution of the same concentration as used for the measurement of oxygen overvoltage.

The results are tabulated below and V—log *i* curves for different cases are shown in Fig. 1. Usually the results were reproducible to within

TABLE I

Hydrogen overvoltage in aqueous solutions of HF and other acids at 25° C.

Current Density in milliamp /sq. cm.	Hydrogen overvoltage in centivolts														
	N H_2SO_4 acid	N HF acid	N Formic acid	N Acetic acid	N/5 HF acid										
	Pt	Pt	Pt	Pt	Pt	Platinized Pt	Ag	Fe	Ni	Cr	Au	Cu	Co	Zn	Al
0·05	—	0	—	—	0	—	—	—	—	—	—	—	—	—	—
0·1	—	1	—	—	1	0	24	24	32	39	26	44	48	60	63
0·2	0	2	2	6	4	—	28	—	38	—	33	51	53	—	—
0·3	—	4	3	10	6	½	30	25	42	40	37	55	57	61	64
0·5	0	7	5	15	11	—	33	—	47	—	42	60	61	—	—
1·0	1	10	9	22	18	2	38	26	54	44	48	66	67	65	65½
2·0	2	14	14	30	24	—	41	—	60	—	56	74	73	—	—
3·0	—	17	17	40	29	5	45	34	64	56	60	78	77	77	67
5·0	4	25	20	67	37	—	53	—	74	—	68	88	82	—	—
10·0	6	40	28	—	56	16	68	60	95	76	80	110	95	99	81
20·0	9	—	—	—	—	—	—	—	—	—	—	—	—	—	—
50·0	13	—	—	—	—	—	—	—	—	—	—	—	—	—	—
100·0	18	—	—	—	—	—	—	—	—	—	—	—	—	—	—

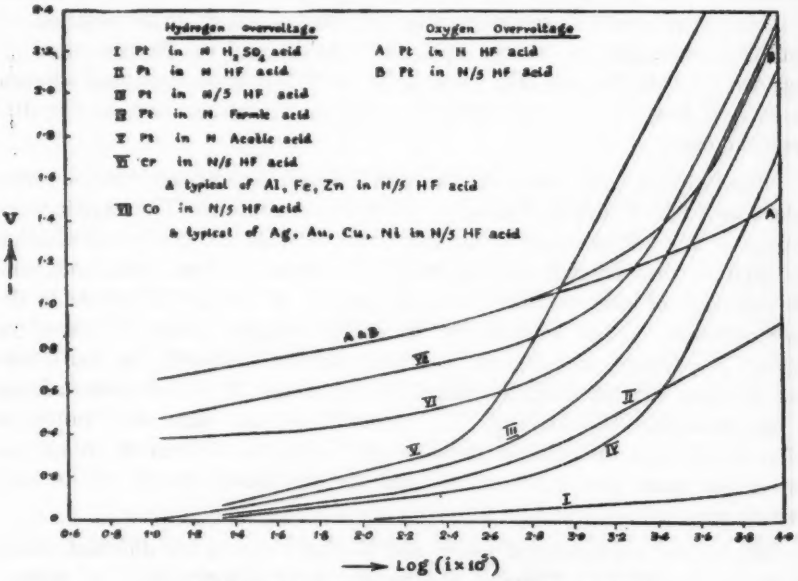
Hydrogen overvoltage
I Pt in N H_2SO_4 acid
II Pt in N HF acid
III Pt in N/5 HF acid
IV Pt in N Formic acid
V Pt in N Acetic acid
VI Cr in N/5 HF acid
a typical of Al, Fe, Zn in N/5 HF acid
VII Co in N/5 HF acid
a typical of Ag, Au, Cu, Ni in N/5 HF acid
Oxygen Overvoltage
A Pt in N HF acid
B Pt in N/5 HF acid
V
Log (i x 10⁵)

FIG. 1. Hydrogen and Oxygen overvoltages at 25°C.

$\pm$ 0·002 v. to $\pm$ 0·02 v. (varying from the lowest to the highest c.d. used), although sometimes, specially at the higher current densities, the reproducibility was much poorer. Moreover, very nearly the same values were obtained on different samples of the same metal prepared in the same way. The reproducibility at any c.d. was, however, different for different metals.

Discussion

The linear relation, $V = a + b \log i$, between overvoltage and the logarithm of current density is found to hold good below current densities of about 0·005 amp./sq. cm., but at greater current densities the overvoltage

Table II

Oxygen overvoltage on Pt in aqueous solution of HF acid at 25° C.

Current density in milliamp./sq. cm. →	0·05	0·1	0·2	0·4	0·6	1·0	1·5	2·0	6·0
Overvoltage in centivolts—									
N HF acid ..	61	66	71	77	80	84	86	89	103
N/5 HF acid ..	60	66	71	76	79	83	86	89	103

Table III

Values of b *in the Tafel equation* $V = a + b \log i$

Hydrogen overvoltage										Oxygen overvoltage	
N H_2O_4 acid	N HF acid	N Formic acid	N Acetic acid	N/5 HF acid						N HF acid	N/5 HF acid
Pt	Pt	Pt	Pt	Pt	Au	Cu	Ni	Co	Ag	Pt	Pt
0·10	0·145	0·15	0·235	0·215	0·23	0·225	0·23	0·20	0·135	0·175	0·175

values are increasingly higher than required by this relation. This deviation from linearity may be due to (i) concentration overpotential, and/or (ii) resistance overpotential being included in the measured potential.[2, 3] The former does not seem to be included in measurements even at these current densities, since increasing the speed of rotation of the polarised electrode above that at which measurements were made (about 2000 r.p.m.) did not produce any significant effect in the measured potential. From the following considerations, however, it appears reasonable to attribute this deviation to the inclusion of resistance overpotential in the measured potential. Thus, the differences between the measured potentials at these current

densities and the corresponding values obtained by extrapolating the initial straight portions of the V—log *i* curves to the higher c.d. region are almost in the same ratio as the current densities themselves. Values for these current densities in N HF acid are lower than those in N/5 HF acid in the case of hydrogen as well as oxygen overvoltage. Platinized Pt which is known to have a very small overvoltage even at very high current densities also showed an enormously increasing overvoltage in N/5 HF acid solution at current densities higher than 5 milliamp./sq. cm. as observed in the case of other surfaces. In the case of sulphuric acid, deviation of the above type was almost unnoticeable even at current densities ten times as great as that in the case of hydrofluoric acid. This is quite consistent with the much larger hydrogen-ion concentration and conductivity of N sulphuric acid as compared to those of N or N/5 HF acid solution. On account of comparatively weak ionisation in N or N/5 HF acid, inclusion of resistance overpotential in measurements is, in fact, not unexpected even at current densities as low as 5 milliamp./sq. cm. in view of the method of measurement employed. Owing to the presence of this complicating factor results at current densities upwards of that mentioned above hardly deserve to be listed in the table and hence are shown graphically only; this also made it superfluous to take readings at current densities higher than 1×10^{-1} amp./sq. cm.

In the case of Pt deviation from the linear V—log *i* relation occurs in the low c.d. region also (*cf.* Fig. 1). As pointed out by Bowden and Agar[2] this is due to the rate of electrosolution of hydrogen being comparable to that of its electrodeposition under the conditions prevailing in the present case.

The slopes of V—log *i* graphs, *i.e.*, the values of *b* occurring in the overvoltage equation $V = a + b \log i$ are very small in the case of hydrogen overvoltage on Fe, Cr, Al and Zn. This is due to the fact that the low polarisation under which this effect is observed is not sufficient to overcome the spontaneous chemical reaction between these metals and HF acid.[13] The consequent spontaneous evolution of hydrogen in quantities much greater than that due to the polarisation upsets the electrochemical equilibrium so that the measured polarisation potential is almost independent of c.d. in this region. Moreover, due to spontaneous chemical attack, the metal surface gets covered with a layer of the corresponding fluoride by which the nature as well as the physical condition of the surface gets changed so that the values measured would not refer to the metal surfaces themselves.

The values of *b* for other cases are given in Table III. It is evident that except for hydrogen overvoltage on Pt in N solution of sulphuric and

hydrofluoric acids, the values of b for hydrogen as well as oxygen overvoltage are, in general, about twice the value usually obtained in other cases by other workers. As pointed out by Bowden[4] this may be ascribed to the fact that hydrogen-ion concentration being low in the case of N/5 HF acid, the solution layer next the electrode gets depleted of hydrogen ions; moreover, the conductivity of N/5 HF acid is itself low; under these conditions the measured potential includes an appreciable fall of potential in the solution. For hydrogen overvoltage on Pt in N HF acid, however, the value of b is not far removed from the usual value; but, even in this case, absolute overvoltage values are higher than in N sulphuric acid (Table I) or in other concentrations of sulphuric acid, hydrochloric acid, etc., studied by other workers. This is due to the fact that although hydrogen-ion concentration and conductivity of N solution are greater than those of N/5 solution of HF acid, these are still not enough for the results to be independent of slight resistance errors. The hydrogen overvoltage values obtained in the case of N formic and acetic acids are also in conformity with the above view. Formic acid, having the same order of ionisation as hydrofluoric acid in N solutions, gives results similar to hydrofluoric acid; while N acetic acid with much weaker ionisation gives a higher value for b than is the case with N HF acid. Moreover, deviation from linearity occurs much earlier and is much greater in N acetic acid than in N hydrofluoric acid.

From Table I it is evident that hydrogen overvoltage values in N/5 solution are greater than in N solution of HF acid. This apparent variation of overvoltage with concentration may also be explained in a similar way. In the case of oxygen overvoltage the values at the two concentrations of HF acid are the same in the initial stages where the Tafel equation is obeyed.

It thus appears that results obtained with HF acid solutions are fundamentally similar to those obtained with other acids, the deviations found being only apparent and attributable to causes arising from weak ionisation of HF acid.

The nature of the two breaks occurring in the current voltage curves for the electrolysis of aqueous solutions of alkali fluorides and ammonium fluoride between bright Pt electrodes[6, 14] can now be considered in the light of these results. The first break occurs at a c.d. of about 0·06 milliamp./sq. cm., and the second break at a c.d. of about 0·7 milliamp./sq. cm. In the first instance, as is evident from Tables I and II the measured potential even for the first break must include an oxygen overvoltage value, although the hydrogen overvoltage at this c.d. is negligible. Again in passing from lower to higher c.d. in this range, hydrogen overvoltage on Pt in N HF acid

increases by 0·08 v. and oxygen overvoltage increases by 0·19 v. The total increase of overvoltage at the two electrodes is therefore 0·27 v. This is much lower than the difference between the potentials for the two breaks which is at least 0·60 v. taking Crockford and Loftin's figures,[6] and 1·0 v. from the present author's results.[14] Due to the greater ionisation and conductivity of salt solutions the hydrogen and oxygen overvoltages in these solutions are expected to be somewhat lower than reported here for N HF acid. The electrode process at the second break cannot, therefore, be regarded as a duplication of that at the first break, namely, the primary decomposition of water, and differing from it merely by the inclusion of increased values for the hydrogen and oxygen overvoltages in the measured potential for the second break. This is quite in conformity with the conclusions already arrived at with regard to the nature of the second break from other considerations. The nature of the reactions at the second break, however, merits further work if more light is to be gained on the point, and work in this direction is in progress.

In conclusion the author wishes to express his indebtedness to the C.P. Government for a research scholarship which enabled him to undertake this investigation, and to Dr. A. N. Kappanna of the College of Science, Nagpur, for invaluable help and advice during the course of the work. To Sir J. C. Ghosh, Director of the Indian Institute of Science, Bangalore, the author owes a deep debt of gratitude for the interest taken in this work and facilities provided.

Summary

Hydrogen overvoltage measurements have been made at 25° C. at current densities ranging from 5×10^{-5} to 1×10^{-1} amp./sq. cm. on platinized Pt, Pt, Ag, Fe, Ni, Cr, Au, Cu, Co, Zn and Al in oxygen-free N/5 aqueous solution of HF acid, and on Pt only in N solutions of HF, H_2SO_4, formic and acetic acids. Oxygen overvoltage has been determined on Pt at 25° C. at current densities ranging from 5×10^{-5} to 6×10^{-3} amp./sq. cm. in N and N/5 aqueous solutions of HF acid. Except Pt, Ag, and Al, the metals were used in electro-deposited form. Reproducibility of results varied from $\pm 0{\cdot}002$ v. to $\pm 0{\cdot}02$ v. according to current density. At current densities below 5 milliamp./sq.cm. the linear relation $V = a+b \log i$ between overvoltage and current density is found to hold good. For hydrogen overvoltage $b = 0{\cdot}20$ to $0{\cdot}23$ for non-attackable metals in N/5 solution and 0.145 for Pt in N solution of HF acid; for attackable metals the value of b is very small. For oxygen overvoltage on Pt in N and N/5 solutions of HF acid $b = 0.175$. At current densities upwards of 5 milliamp./sq.cm. the measured potential becomes increasingly larger than

required by this relation. From an examination of the results obtained it appears that the behaviour of HF acid with respect to overvoltage phenomenon is essentially the same as those of H_2SO_4 and other similar acids, the observed departures being attributable to causes arising from weak ionisation of HF acid. Results for hydrogen and oxygen overvoltages on Pt indicate that the second break in the electrolysis of alkali and ammonium fluoride solutions may be due to electrode processes other than the primary decomposition of water.

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KAMALA DYE AS AN ANTHELMINTIC

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For nearly a century, kamala has enjoyed a reputation as an anthelmintic. But in scientific literature, reports about its efficacy have been conflicting. Semper[1] tested the drug on frogs, tadpoles and worms and found that it was definitely toxic. Caius and Mhaskar[2] found it useless against hook worms, ascarids and whipworms and stated that it could not be recommended as an anthelmintic. Beach and Warren[3] on the other hand found it to be a good teniacide for chicken. One of the possible reasons for the above-mentioned differences appears to be due to the large variation in the quality of the material employed.

The British Pharmacopœia (old editions) and B. P. Codex, 1934, specify kamala by means of its microscopic characters and its ash content. In our examination of a large number of samples obtained from various places in India, we found that they had all the required microscopic characters but are highly variable with regard to their ash content. The best of them agreed with the Pharmacopœial limit of 4–5% ash but in most of them, the ash varied from 15–40%. As a matter of fact, Perkin[4] found an ash content of 52·5% for the sample of kamala which he analysed. As high values as 87·3% have also been reported for some commercial samples.[5] High ash is a definite indication of poor quality which may arise as the result of bad processing in the course of collection, allowing red earth and sand to come in, or due to wilful adulteration with ferruginous earth. The quality of kamala could however be considerably improved by garbling. We find that it is much more efficient to adopt flotation and thereby the ash content could fairly easily be brought down to 5%.

The above result would suggest that the impurity in kamala is mostly of inorganic origin. But it need not always be so. For assessing the quality of kamala more correctly it may be necessary to examine it for the active principles and estimate them. Chemical studies have indicated that the chief crystalline component of kamala is rottlerin. The yield of this substance could therefore give information about the quality of kamala. Though Laube[6] and Oettingen[7] failed to get any crystalline components from the kamala samples analysed by them, in our investigation, all the samples that we examined yielded rottlerin. Those that were purified by flotation and that had the B.P. limit for ash, generally gave a yield of 10%

of rottlerin when extracted in the following manner. One gram of the drug was successively boiled with 15 c.c., 10 c.c., and 10 c.c. of benzene for 5 minutes each time and filtered. The combined filtrate was concentrated to 5 c.c. and allowed to stand for 4 hours, when rottlerin separated out as a red crystalline powder. The yield of rottlerin obtained by this method of extraction could be taken as a rough indication of quality for even the crude samples of kamala. It appears possible that the cases where rottlerin was not obtained could be explained as due to unsuitable methods of extraction because rottlerin is easily susceptible to oxidation and leads to the formation of uncrystallizable substances. But this method of extraction is not suitable for correct quantitative assay.

Recently, a proposal has been made for the chemical assay of kamala by treatment of an ether extract of the drug with baryta, acidifying the alkaline solution and again extracting it with ether. The ether is distilled off and the residue is weighed.[8] This method is analogous to the chemical method of assay suggested for the male fern. As in the case of male fern it is obviously not suitable for kamala too, since rottlerin undergoes decomposition under these conditions and inert resinous matter also dissolves in ether and baryta.

In the absence of a precise chemical method, a biological method of assay seemed to offer promise. In order to test the use of fish for this purpose, experiments have now been conducted employing pure rottlerin and extracts of kamala. The fish used are small ones locally available (*Haplochilus panchax*) and the time taken for the fish to lose balance is adopted as the criterion of toxicity according to the original suggestion of Krishnaswami and Seshadri.[9] Besides rottlerin, its methyl ether has also been tested, since in the case of hydroxy-flavones, the methyl ethers are much more toxic than the original hydroxy compounds. The results obtained are given below. An alcoholic solution (less than 10 c.c) of the particular substance is added to a litre of tap water and thoroughly mixed before introducing the fish (6 in number). In the case of the methyl ether one gram of gelatin was first added to the water in order to keep the substance in clear solution.

No.	Name of the Substance	Concentration m. grams/litre	Turning time	Remarks
1	Rottlerin	15	85 min.	Died very soon after removal to fresh water
2	,,	30	37 ,,	,,
3	,,	50	30 ,,	,,
4	Rottlerin methyl ether	5	Unaffected in 24 hours	Acquired brown colour which faded gradually
5	,,	10	,,	,,
6	,,	30	Found dead overnight	,,

It will be clear from the above results that rottlerin is definitely toxic and is an efficient anthelmintic. It should be noted that the fish used did not recover after the experiment when they were transferred to fresh water but died within a minute after turning upside down. This is experienced only with some of the most potent insecticides. The methyl ether is unexpectedly much weaker. In this respect, rottlerin differs from the hydroxy-flavones.

It is possible that rottlerin, at any rate the quantity isolated, does not account for all the toxicity of kamala. We have, therefore, examined the total benzene extract of kamala before and after the removal of rottlerin and also the subsequent alcoholic extract of the residue left after the benzene extraction. With all these, the effect on the fish is very similar to that of rottlerin, the details of the reactions of the fish being just the same. It, therefore, follows that the other toxic components present are very similar to rottlerin, and that the potency of the samples of kamala could be assessed by comparison with pure rottlerin used as standard. Using this method, the contributions of the various fractions towards the anthelmintic value of kamala could be estimated, taking the toxicity of rottlerin as one as explained below.

One gram of kamala was extracted exhaustively by boiling for 5 minutes each time with 15 c.c., 10 c.c., 10 c.c., and 10 c.c. of benzene and the total extract evaporated to dryness; yield 0·6 gram. This was taken up in 30 c.c. of rectified spirit. 2 c.c. of this solution (40 mg. of extract) when added to one litre of water was found to have the same toxicity as 16·5 mg. of rottlerin in the same volume of water. 4 c.c. of the solution (80 mg.) and 5 c.c. of the solution (100 mg.) were equal to 33 and 41·5 mg. of rottlerin. Thus the benzene extract had 0·4 of the toxic intensity of pure rottlerin. Since 10% of total kamala or $\frac{1}{8}$ of benzene extract can be separated out as rottlerin, the total anthelmintic potency of the benzene extract is $2\frac{1}{2}$ times the contribution made by the isolable rottlerin itself. The non-rottlerin portion of the benzene extract (50% of original kamala) accounts for the remaining $1\frac{1}{2}$ and this has about 0·3 of the toxic intensity of kamala.

The subsequent alcoholic extract is about 15% of the benzene insoluble residue and thus, it is 6% of the original kamala. This extract is also toxic; but 100 mg. of it are only equal to 10 mg. of rottlerin in toxicity. Its potency is thus only 1/10 that of rottlerin and since further this portion is small, it contributes very little to the total anthelmintic value of kamala (about 2·5%).

It could therefore be concluded that though the total anthelmintic value of kamala may not be due to rottlerin alone and may be due to the other components, rottlerin constitutes the most important and powerful toxic component of kamala. Weight for weight the best quality of kamala has less than a third of the toxicity of pure rottlerin.

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NUCLEAR OXIDATION IN THE FLAVONE SERIES

Part VII. Oxidation of Baicalein and Scutellarein

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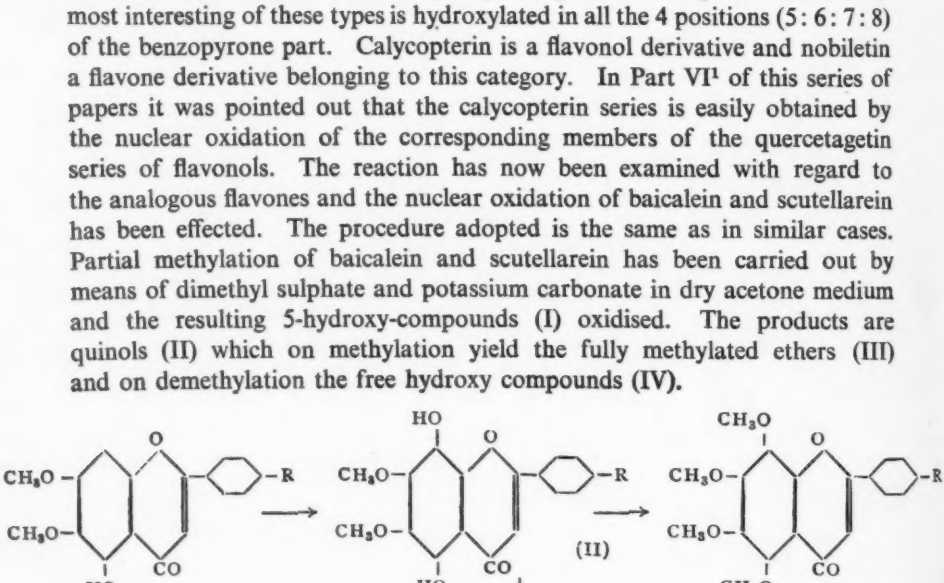
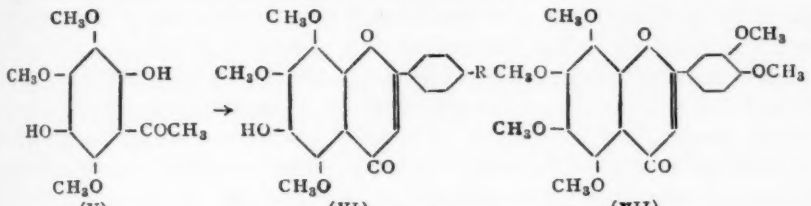
A marked difference between anthoxanthins and anthocyanins is in the number of states of oxidation and of methylation in which they occur in nature. The former exhibits an enormously large range in this respect. One of the most interesting of these types is hydroxylated in all the 4 positions (5 : 6 : 7 : 8) of the benzopyrone part. Calycopterin is a flavonol derivative and nobiletin a flavone derivative belonging to this category. In Part VI[1] of this series of papers it was pointed out that the calycopterin series is easily obtained by the nuclear oxidation of the corresponding members of the quercetagetin series of flavonols. The reaction has now been examined with regard to the analogous flavones and the nuclear oxidation of baicalein and scutellarein has been effected. The procedure adopted is the same as in similar cases. Partial methylation of baicalein and scutellarein has been carried out by means of dimethyl sulphate and potassium carbonate in dry acetone medium and the resulting 5-hydroxy-compounds (I) oxidised. The products are quinols (II) which on methylation yield the fully methylated ethers (III) and on demethylation the free hydroxy compounds (IV).



For purposes of comparison, synthesis of compounds (III) and (IV) has also been effected independently starting from the ketone[2] (V) and adopting the Allan-Robinson method. This direct condensation seems to be more convenient for getting these compounds than the Baker-Venkataraman procedure adopted by Horii[3] for the synthesis of nobiletin (VII). The 6-hydroxy compounds (VI) first formed yield (III) when subjected to methylation and (IV) when demethylated. The samples of (III) and (IV) obtained by the two methods are found to be identical.



Dihydroxy compounds of type (II) are yellow crystalline solids giving the characteristic reactions of similarly constituted quinols. With sodium hydroxide they form brown red solutions. When a drop of ferric chloride is added to an alcoholic solution a deep greenish blue colour is obtained and this is fairly stable. On long standing or adding excess of the reagent it turns deep brownish red. The 6-hydroxy-compounds (VI) are also yellow substances dissolving in alkali to form yellow solutions. They do not give colour with ferric chloride. The fully methylated flavones (III) are colourless solids which crystallise best when free from moisture; anhydrous solvents should therefore be used for this purpose. They dissolve in strong mineral acids forming yellow solutions; no fluorescence is found in sulphuric acid solutions. They are characterised by the readiness with which they give bright red colour with magnesium and hydrochloric acid in alcoholic solution. The corresponding free polyhydroxy flavones (IV) give only orange red colours in this reaction. They are bright yellow substances which dissolve in sulphuric acid with a red colour and no fluorescence. The two described in this paper do not yield prominent colour changes in buffer solutions. The tetrahydroxy-compound prepared from baicalein resembles it in giving a stable greenish blue precipitat : in alkali, whereas with the higher member the initial blue precipitate subsequently dissolves.

Experimental

Baicalein-dimethyl-ether (*I*, $R = H$)

This was prepared by the partial methylation of baicalein using dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium. A

more convenient procedure is to use the mixture of baicalein and oroxylin—A that can be obtained from the bark of *Oroxylum indicum* as described below.

A solution of the mixture (2 g.) in anhydrous acetone (50 c.c.) was treated with dimethyl sulphate (1·2 c.c.) and anhydrous potassium carbonate (10 g.). After refluxing for 6 hours the solvent was distilled off and the residue treated with water. The yellow solid left behind was filtered, washed well with water and dried. Crystallisation from alcohol (with a few drops of glacial acetic acid) yielded pale yellow rectangular plates melting at 156–57°. Yield 1·5 g. (Bargellini[4] gave the m.p. 155–56°). When in some experiments appreciable quantities of the trimethyl ether were also formed the mixture was dissolved in absolute alcohol, treated with just enough potash, and evaporated. The solid residue was washed well with hot benzene to remove the trimethyl ether. The remaining potassium salt was decomposed with dilute hydrochloric acid and the product crystallised.

5 : 8-*Dihydroxy*-6 : 7-*dimethoxy-flavone* (*II*, $R = H$)

A stirred solution of the above dimethyl ether (1 g.) in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (1·5 g. in 25 c.c.) was treated dropwise with a solution of potassium persulphate in water (1·5 g. in 50 c.c.) in two hours. The greenish brown solution was allowed to stand for 24 hours, just acidified with hydrochloric acid and the precipitated solid filtered off. The filtrate was extracted twice with ether to recover completely the unchanged dimethyl ether of baicalein, treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (25 c.c.) and kept in a boiling water-bath for 30 minutes. The glistening yellowish brown crystalline solid that separated out was filtered after cooling, washed and purified by recrystallising from a mixture of ethyl acetate and petroleum ether when it appeared as golden yellow broad rectangular plates melting at 181–82°. (Found: C, 64·9; H, 4·2; $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%.) Yield 0·35 g. It was sparingly soluble in alcohol and the solution gave an intense bluish green colour with a drop of ferric chloride and with a few more drops the colour changed to dark brown. In aqueous sodium hydroxide it readily dissolved to a dark red solution.

The dihydroxy compound (0·1 g.) was acetylated using acetic anhydride (3 c.c.) and a drop of pyridine. The acetate crystallised from alcohol in the form of colourless needles melting at 172–73°.

5 : 6 : 7 : 8-*Tetramethoxy-flavone* (*III*, $R = H$)

A solution of the dihydroxy compound (II) (0·2 g.) in anhydrous acetone (25 c.c.) was treated with dimethyl sulphate (0·5 c.c.) and potassium carbo-

nate (5 g.). After refluxing for 6 hours the potassium salts were filtered off and the residue washed with hot acetone. The filtrate was distilled to recover the solvent and treated with water when a colourless solid separated out. It was filtered, washed with aqueous sodium hydroxide followed by water, dried and purified by crystallisation from ligroin. It came out in the form of colourless narrow rectangular plates melting at 117–18° (Found: C, 66·9; H, 5·4; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%). It was readily soluble in common organic solvents, insoluble in aqueous sodium hydroxide and did not give any colour with alcoholic ferric chloride. It gave a deep red colour with magnesium and hydrochloric acid in alcoholic solution. It was identical with the sample obtained by the Allan-Robinson method described later and the mixed melting point was undepressed.

5:6:7:8-*Tetrahydroxy-flavone*: (6:8-*dihydroxy chrysin*) (*IV*, $R = H$)

The above dihydroxy-compound (II, R = H) (0·3 g.) was dissolved in acetic anhydride (5 c.c.) and the solution cautiously treated with hydriodic acid (8 c.c.). The mixture was gently refluxed for 1 hour, cooled and poured into water (100 c.c.). Sufficient sodium sulphite was added to remove the iodine present. The orange yellow solid product was filtered and washed well with water. It crystallised from ethyl acetate in the form of glistening orange yellow stout rectangular prisms melting with decomposition at 275–77°. (Found: C, 62·7; H, 3·2; $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%.) It was sparingly soluble in acetone and ethyl acetate but more easily in alcohol. In alcoholic solution it gave an intense blue colour with a drop of ferric chloride and this changed to brown red with excess of the reagent. With *p*-benzoquinone the solution in absolute alcohol became deep red and soon faded to yellow. With 5% sodium hydroxide a deep brown red solution was obtained along with a blue precipitate; on shaking with air the colour of the solution changed to greenish yellow and then pale green. In 5% sodium carbonate the solid substance turned first red and then formed a deep brown solution with a blue precipitate; the colour of the solution changed to pale green the precipitate being unchanged. In 5% sodium bicarbonate the solid slowly dissolved to a yellow solution with a blue precipitate and the colour of the solution changed to pale greenish brown. In alcoholic solution a bright orange coloured precipitate was obtained with lead acetate.

The tetrahydroxy flavone (0·1 g.) was acetylated using acetic anhydride (5 c.c.) and a drop of pyridine. The acetate crystallised out from absolute alcohol in the form of colourless rectangular plates melting at 215–17°.

Scutellarein-trimethyl-ether (*I*, $R = OCH_3$) was made by the partial methylation of scutellarein adopting the procedure described for baicalein-dimethyl-ether. It was dull yellow in colour and melted at 189–90°.

5:8-*Dihydroxy*-6:7:4′-*trimethoxy-flavone* (*II*, $R = OCH_3$)

A solution of the above trimethyl-ether of scutellarein (1 g.) in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (2 g. in 25 c.c.) was gradually treated with stirring with a solution of potassium persulphate (2 g. in 50 c.c.) during the course of two hours. The dark brown solution was kept for 24 hours and the product worked up as described already for the similar case. On crystallisation from alcohol it separated out as bright yellow short needles melting at 250–51° with decomposition (Found: C, 59·3; H, 5·0; $C_{18}H_{16}O_7$, H_2O requires C, 59·7; H, 5·0%). It gave the same reactions as the corresponding compound obtained from baicalein dimethyl ether; yield 0·3 g.

5:6:7:8:4′-*Pentamethoxy-flavone* (*III*, $R = OCH_3$)

The above dihydroxy compound (0·1 g.) was methylated in anhydrous acetone solution (20 c.c.) with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (5 g.). The methyl ether crystallised out from dry ethyl acetate as colourless long rectangular prisms and rods melting at 150–51° alone or in admixture with the sample obtained by the Allan-Robinson method. (Found: C, 64·2; H, 5·5; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%.) Its reactions were quite similar to those of the tetramethoxy-compound (III, R = H) described earlier.

5:6:7:8:4′-*Pentahydroxy-flavone* (6:8-*dihydroxy-apigenin*) (*IV*, $R = OH$)

The dihydroxy compound (II, $R = OCH_3$) (0·1 g.) was demethylated using acetic anhydride and hydriodic acid. The penta-hydroxy-flavone (6:8-dihydroxy-apigenin) crystallised from ethyl acetate in the form of yellow plates melting at 318° with decomposition. (Found: C, 59·6; H, 3·3; $C_{15}H_{10}O_7$ requires C, 59·6; H, 3·3%.) With ferric chloride in alcoholic solution an intense blue colour was obtained which rapidly changed to brown with a little excess of the reagent. With *p*-benzoquinone in alcoholic solution a deep red colour was obtained which changed to yellowish brown. In 5% sodium carbonate the flavone quickly dissolved to a brown red solution with a small amount of a blue precipitate which however dissolved slowly and the solution changed its colour to pale brownish yellow. In 5% sodium hydroxide it quickly dissolved to deep brown red solution rapidly going to pale greenish brown and finally pale yellow.

5:7:8-*Trimethoxy*-6-*hydroxy-flavone* (*VI*, $R = H$)

An intimate mixture of the ketone[2] (V) (1·2 g.), benzoic anhydride (9 g.) and sodium benzoate (5 g.) was heated under reduced pressure at 180–85° for 4 hours. The product was refluxed with 10% alcoholic potash (60 c.c.) for 30 minutes. The solvent was distilled off under reduced pressure, the residue dissolved in water and the clear brown solution saturated with carbondioxide. It was then extracted with ether, the extract dried over sodium sulphate and distilled. The yellow crystalline solid left behind was crystallised from alcohol when it separated out as golden yellow rectangular plates melting at 178–79°. (Found: C, 65·8; H, 5·1; $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%). Yield 0·2 g. It dissolved in sodium hydroxide to a bright yellow solution and did not give any colour with ferric chloride in alcoholic solution.

Methylation of the above flavone (0·1 g.) in anhydrous acetone (20 c.c.) with dimethyl sulphate (0·2 c.c.) and potassium carbonate (2 g.) yielded the methyl ether which crystallised from ligroin in the form of colourless narrow rectangular plates melting at 117–18°. Mixed melting point with the sample obtained by the nuclear oxidation followed by methylation of baicalein dimethyl ether was not depressed.

Demethylation of the 6-hydroxy compound (VI) in the usual manner with hydriodic acid yielded the tetrahydroxy-flavone (6: 8-dihyrdoxy-chrysin) which crystallised from dry ethyl acetate in the form of golden yellow stout rectangular prisms melting at 275–77° with decomposition. It was identical with the sample prepared by the method of nuclear oxidation from baicalein in all its properties and reactions.

6-*Hydroxy*-5:7:8:4′-*tetramethoxy-flavone* (*VI*, $R = OCH_3$)

The ketone (1·5 g.) (V) was condensed with anisic anhydride (10 g.) and sodium anisate (3 g.) under the conditions already described. The flavone crystallised from alcohol as golden yellow triangular plates melting at 199–200°. Yield 0·3 g. (Found: C, 64·2; H, 4·8; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%.). It dissolved to a yellow solution in aqueous sodium hydroxide and in alcoholic solution it did not give any colour with ferric chloride.

Methylation of the above flavone (0·3 g.) was done in dry acetone (20 c.c.) with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (5 g.). When crystallised from dry ethyl acetate, the pentamethyl ether separated out in the form of colourless needles and prismatic rods melting at 150–51°. Mixed melting point with the sample prepared by the

nuclear oxidation of scutellarein was not depressed. Yield 0·2 g. (Found: C, 64·8; H, 5·6; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%). The pentamethoxy flavone was insoluble in aqueous sodium hydroxide and did not give colour with ferric chloride. In alcoholic solution it readily gave a deep red colour with magnesium and hydrochloric acid.

Demethylation of the 6-hydroxy flavone (VI) in acetic anhydride solution with hydriodic acid yielded the pentahydroxy flavone (6 : 8-dihydroxy apigenin) which crystallised out from ethyl acetate in the form of bright yellow plates melting with decomposition at 318° identical with the sample prepared by the nuclear oxidation of scutellarein described before.

Summary

Nuclear oxidation of baicalein and scutellarein takes place readily in the 8-position, the partial methyl ethers being employed. Further methylation yields fully methylated ethers of the nobiletin series and demethylation the corresponding nor-compounds. For purposes of comparison these substances have also been prepared from 2 : 5-dihydroxy-3 : 4 : 6-trimethoxy acetophenone by the Allan-Robinson method. The characteristic properties and reactions of these compounds are described.

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SYNTHESIS OF 5-HYDROXYFLAVONOLS

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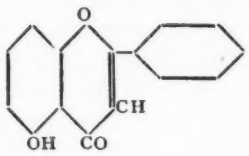
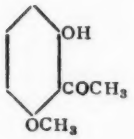
Among the naturally occurring flavones and flavonols, the most numerous group contain the 5: 7-arrangement of hydroxyl groups in the benzopyrone part[1] and these seem to be the most fundamental of the anthoxanthins from the point of view of biogenesis. There are, however, a few compounds with a single hydroxy group in the 7-position, the 5-position being unsubstituted. The flavone, pratol and the flavonols, fisetin and robinetin belong to this type. On the other hand, till very recently no compound with a hydroxyl only in the 5-position and none in the 7-position was known to occur in nature. 5-Hydroxy-flavone (I) was isolated by Karrer and Schwab[2] from a deposit on the stalks and blossoms of *Primula imperialis* var. *gracilis* which consisted mainly of simple flavone along with some 5-hydroxy-flavone. The synthesis of this hydroxy-flavone had been accomplished by Sugasawa[3] several years earlier starting from γ-resacetophenone and adopting the Allan-Robinson method. Improvements in the preparation have recently been described.[4] The earlier synthesis helped in the identification of the compound in the plant material. The occurrence of flavonols of this type in nature also seems to be possible. It is therefore desirable to have records of the properties of synthetic samples so that their identification in natural products may be easy. With this end in view some members of this group have now been prepared and their properties described in this paper.



(I)



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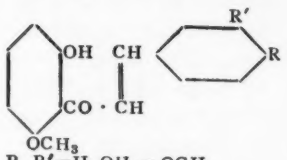


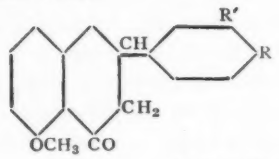
R, R′=H, OH or OCH_3

(III)

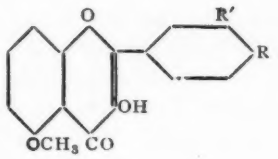
For the synthesis of 5-hydroxy flavonols the method of Allan and Robinson is not suitable since the required ω-methoxy-γ-resacetophenone has not yet been made. Hence the older method of Kostanecki has been employed, 2-acetyl resorcinol being the starting material. For the first stage in the synthesis, that is the chalkone condensation, it is found desirable to use an

excess of the aldehyde component and to methylate as far as possible the hydroxyl groups in both the components employed. Thus 2-acetyl resorcinol does not undergo appreciable condensation with vanillin; its condensation with benzaldehyde and veratric and anisaldehydes is better but the yields are poor. Very satisfactory yields of chalkones (III) are obtained by employing these aldehydes and the monomethyl ether of 2-acetyl resorcinol (II). As in many similar cases the products of these condensations contain some quantity of the corresponding flavanones (IV). Further conversion into the flavanones is effected by boiling the chalkones with alcoholic sulphuric acid. Even here the products are mixtures of flavanones and chalkones and have to be separated. The preliminary methylation of hydroxyl groups already mentioned is of advantage for effecting this separation easily by means of cold aqueous alkali, the chalkones being soluble and the flavanones insoluble. The chalkones are coloured, yellow to orange red, whereas the flavanones are colourless. The latter readily yield red solutions in alcohol when reduced with magnesium and hydrochloric acid.

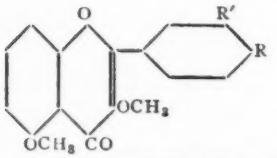
The fully methylated flavanones (IV) are converted into the flavonols (V) in one stage according to the method of Row and Seshadri[5] in which the yields are better and the products more readily obtained pure. Further methylation yields the methyl ethers (VI) and demethylation the hydroxy compounds (VII).



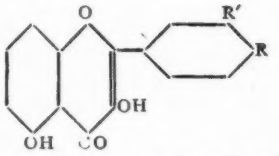
(IV) R, R′ = H or OCH_3



(V)



(VI) R, R′ = H or OCH_3



(VII) R, R′ = H or OH

The 3-hydroxy compounds (V) are yellow substances exhibiting a weak green fluorescence in neutral alcoholic and concentrated sulphuric acid solutions, the colour of the solutions being yellow. They give an olive green colour with alcoholic ferric chloride. The fully methylated compounds (VI) do not exhibit any fluorescence in the above solvents. The hydroxy-flavanols (VII) are yellow in colour and give an olive-green colour

with ferric chloride and do not exhibit fluorescence in solution. In contrast to these the 7-hydroxy flavonols exhibit marked fluorescence. Thus the 5-hydroxyl is inhibitive of fluorescence; conversion of this into the methoxyl gives rise to some weak fluorescence as in compounds of type (V). Similar effects have been noted in the group of pyrylium salts and coumarins also.[6] In general the 7-hydroxy compounds have markedly higher melting points than the corresponding 5-hydroxy flavonols.

Experimental

2-Hydroxy-6-methoxy-chalkone (*III*, *R*, *R'* = *H*)

Monomethyl-γ-resacetophenone[7] (1 g.) and benzaldehyde (3 g.) were dissolved in alcohol (20 c.c.) and to the solution aqueous potassium hydroxide (20 c.c.; 50%) was added with shaking at the laboratory temperature. The mixture was kept in a closed container for about 72 hours. The red solution was then diluted with water, ether extracted to remove the unreacted benzaldehyde and then acidified with dilute hydrochloric acid. The reddish brown viscous liquid that separated out was ether extracted and the ether solution washed with sodium bicarbonate (5%) to remove benzoic acid. On removing the ether, the chalkone was obtained as a viscous red liquid which solidified during the course of several days. Final purification was effected by crystallisation from alcohol when it came out as pale yellow rectangular plates and prisms melting at 127–29°; Yield 1·2 g. The product dissolved easily in dilute alkali giving rise to an orange red solution and gave a dark brown colour with alcoholic ferric chloride (Found: C, 75·5; H, 5·6; $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

5-Methoxy-flavanone (*IV*, *R*, *R'* = *H*)

The above chalkone (III) (2 g.) was dissolved in alcohol (100 c.c. of 50%), treated with concentrated sulphuric acid (3 c.c.) and boiled under reflux for a period of 30 hours. As much of the alcohol as possible was then removed under reduced pressure and the solution diluted with water to about 300 c.c. The liquid that separated out solidified easily on shaking with more water. It was filtered and macerated with dilute sodium hydroxide solution to remove the unreacted chalkone. The pale brown residue was dried and crystallised from ethyl acetate when it came out in the form of colourless rectangular prisms melting at 148–50°. Yield 1·2 g. (Found: C, 75·5; H, 5·8; $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%). It was insoluble in dilute alkali in the cold and did not give any colour with ferric chloride.

5-Methoxy-flavonol (*V*, *R*, *R'* = *H*)

5-Methoxy-flavanone (IV) (0·5 g.) was dissolved in alcohol (15 c.c.), gently boiled and then treated with amyl nitrite (3 c.c.) and concentrated

hydrochloric acid (30 c.c.; d. 1·19) in small quantities during the course of 15 minutes. The solution assumed rapidly a dark red colour and it was allowed to stand for 2 hours. It was then diluted to 200 c.c. and ether extracted. From the ether extract, the flavanol was taken up in dilute sodium hydroxide (1 N). On acidifying the alkaline solution, it was precipitated as an orange red solid. When dried and crystallised from ethyl acetate twice, it appeared as pale yellow rectangular prisms melting at 170–71°; rapid crystallisation yielded yellow flat needles the melting point being the same; Yield 0·4 g. The substance dissolved in dilute sodium hydroxide to give a yellow solution and with alcoholic ferric chloride gave a deep pink colour changing to brown. It exhibited a green fluorescence with a blue tinge in neutral alcoholic solution, the solution being coloured pale yellow. In concentrated sulphuric acid solution, it gave a pale green fluorescence (Found: C, 71·2; H, 5·3; $C_{16}H_{12}O_3$, H_2O requires C, 71·1; and H, 5·2%).

3: 5-*Dimethoxy-flavone* (*VI*, *R*, *R'* = *H*)

The above flavanol (V) was methylated with dimethyl sulphate and anhydrous potassium carbonate in acetone solution by boiling for 10 hours. The product that first separated as a liquid solidified on keeping for about 24 hours and on crystallisation from alcohol appeared as colourless rectangular plates and prisms melting at 160–62°. It was insoluble in dilute alkali and did not give any colour with alcoholic ferric chloride (Found: C, 72·2; H, 5·2; OCH_3, 21·8; $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0; and OCH_3, 21·6%). It did not exhibit any fluorescence in alcoholic or concentrated sulphuric acid solutions.

3: 5-*Dihydroxy-flavone* (*VII*, *R*, *R'* = *H*)

5-Methoxy-flavanol (V) (0·5 g.) was dissolved in acetic anhydride (10 c.c.), treated with hydriodic acid (10 c.c.; d. 1·7) and boiled under reflux for ½ hour. It was then poured into water and the iodine present removed by sulphur dioxide. The precipitated yellow compound was purified by crystallisation from alcohol when it came out as long yellow rectangular plates and prisms, melting at 145–46°. It gave an olive green colour with alcoholic ferric chloride and did not exhibit any fluorescence in alcoholic or concentrated sulphuric acid solutions (Found: C, 70·2; H, 4·9; $C_{15}H_{10}O_3$, H_2O requires C, 70·3; and H, 4·7%). The flavanol dissolved in alkalies to give a golden yellow colour.

The acetate was prepared by boiling the flavanol with acetic anhydride and a few drops of pyridine. It was crystallised from acetone when it came out as colourless tiny rectangular prisms melting at 148–49° (Found: C, 71·0; H, 4·5; $C_{19}H_{14}O_5$ requires C, 70·8; H, 4·3%).

2: 6-*Dihydroxy-4'-methoxy-chalkone*

A solution of 2: 6-dihydroxy-acetophenone (1·0 g.) and anisaldehyde (3 g.) in alcohol (20 c.c.) was treated with alkali (20 c.c. of 50% potash) and the red solution heated to boiling on a water-bath for 15 minutes. It was cooled and kept stoppered tightly for 24 hours. On working up as before, the chalkone was obtained as an orange-red crystalline substance. Purified by crystallisation from alcohol, it came out in the form of yellow rectangular plates melting at 185–86°. Yield 0·3 g. It dissolved easily in dilute sodium hydroxide to give a pale yellow solution, and produced a brown colour with alcoholic ferric chloride (Found: C, 71·3; H, 5·4; $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%).

2-*Hydroxy*-6: 4'-*dimethoxy-chalkone* (*III*, $R = OCH_3$, $R' = H$)

Monomethyl-γ-resacetophenone (1 g.) and anisaldehyde (3 g.) were dissolved in alcohol (20 c.c.) and to the solution aqueous potassium hydroxide (30 g. of potash and 20 c.c. of water) was added at the laboratory temperature. The mixture was refluxed on a water-bath for about an hour and then kept tightly stoppered for 24 hours. The chalkone obtained by working up the reaction mixture as before was purified by crystallisation first from dilute alcohol and finally from acetic acid when it came out as bright orange-red needle-shaped crystals melting at 114–15°. Yield 0·8 g. The product dissolved easily in dilute alkali giving rise to an orange red solution and gave a dark brown colour with alcoholic ferric chloride (Found: C, 72·0; H, 5·7; $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%). A better yield (1·12 g.) of this chalkone is obtained by heating the above reaction mixture on a water-bath at 50° for a period of 15 minutes and then keeping the solution tightly stoppered for a period of 60 hours.

5: 4'-*Dimethoxy-flavanone* (*IV*, $R = OCH_3$, $R' = H$)

The above chalkone (III) was converted into the flavanone by boiling a 50% alcoholic solution of the substance with 3% sulphuric acid and worked up as in the previous case. The product was crystallised from ethyl acetate when it came out in the form of colourless flat rectangular plates melting at 115–16°. Yield 0·3 g. (Found: C, 71·4; H, 5·8; $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%). It was insoluble in dilute alkali in the cold, but when boiled with the same, it went into solution giving an orange yellow solution. It did not give any colour with alcoholic ferric chloride.

5: 4'-*Dimethoxy-flavonol* (*V*, $R = OCH_3$, $R' = H$)

The above flavanone (IV) (1 g.) was converted into the flavonol using amyl nitrite and hydrochloric acid as described already. It was purified by crystallisation from ethyl acetate when it came out as yellow narrow

plates tapering at the ends and melting at 171–72°. Yield 0·2 g. (Found: in air-dried sample: C, 64·4; H, 5·4; loss on drying *in vacuo* at 120° for 2 hours 5·3%; $C_{17}H_{14}O_5$, H_2O requires C, 64·6; H, 5·1 and loss on drying 5·7%). It dissolved in dilute sodium hydroxide giving a yellow solution and with alcoholic ferric chloride gave a deep brown colour. It exhibited a green fluorescence with a blue tinge in neutral alcoholic solution, the solution being coloured pale yellow. In concentrated sulphuric acid solution it gave a pale green fluorescence.

3: 5: 4′-*Trimethoxy-flavone* (*VI*, $R = OCH_3$, $R' = H$)

The above flavonol (V) was methylated with dimethyl sulphate and anhydrous potassium carbonate in acetone solution by boiling for a period of 10 hours. The product was worked up as in similar cases and was purified by crystallisation from dilute alcohol when it came out in the form of colourless rectangular plates melting at 141–42°. It was insoluble in alkali and did not give any colour with alcoholic ferric chloride (Found: C, 69·4; H, 5·3; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%).

3: 5: 4′-*Trihydroxy-flavone* (*VII*, $R = OH$, $R' = H$)

5: 4′-Dimethoxy-flavonol (V) was demethylated using hydriodic acid. The yellow product was purified by crystallisation from alcohol when it came out as yellow rectangular plates melting at 214–15°. It gave an olive green colour with alcoholic ferric chloride and did not exhibit any fluorescence in alcoholic or concentrated sulphuric acid solutions (Found: C, 66·4; H, 4·0; $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%). The flavonol dissolved in alkalies to give a golden-yellow colour.

The acetate was prepared by boiling the flavonol with acetic anhydride using a drop of pyridine. The product obtained was crystallised from acetone when it came out as colourless needles and rectangular plates melting at 179–80° (Found: 63·2; H, 4·4; $C_{21}H_{16}O_8$ requires C, 63·4; H, 4·0%).

2:6-*Dihydroxy*-3′: 4′-*dimethoxy-chalkone*

A mixture of 2: 6-hydroxy-acetophenone (1 g.) and veratric aldehyde (3 g.) was dissolved in alcohol (20 c.c.), treated with aqueous potash (30 c.c. of 50%) and the mixture boiled for 15 minutes. It was cooled and kept overnight and the chalkone worked up as before. It was finally purified by crystallisation from alcohol when it came out in the form of orange yellow rectangular plates and prisms melting at 187–88°. Yield 0·6 g. (Found: in air-dried sample: C, 64·4; H, 5·6; loss on drying *in vacuo* at 120° for 2 hours 5·6; $C_{17}H_{16}O_5$, H_2O requires C, 64·2,; H, 5·7; loss on drying 5·7%). The chalkone was easily soluble in ether, alcohol and acetone but

sparingly in benzene and chloroform. It dissolved readily in dilute alkali giving an orange yellow solution and gave a dark brown colour with alcoholic ferric chloride.

2 : 4′-*Dihydroxy*-6 : 3′-*dimethoxy-chalkone*

Mono-methyl-γ-resacetophenone (1 g.) was condensed with vanillin (3 g.) as in the above case. The product was worked up as before and the chalkone was purified by crystallisation from dilute alcohol when it came out in the form of bright orange-red rectangular plates melting at 146–47°. Yield 1·2 g. (Found C, 68·1; H, 5·3; $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%).

2-*Hydroxy*-6 : 3′ : 4′-*trimethoxy-chalkone* (*III*, $R = R' = OCH_3$)

Mono-methyl-γ-resacetophenone (3 g.) was condensed with veratric aldehyde (9 g.) as before and the product obtained was purified by crystallisation from 90% alcohol when it came out as short yellow rectangular plates melting at 131–32°. Yield 4·0 g. (Found: C, 69·0; H, 5·9. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%). It dissolved in alkali giving a deep brown colour and gave a dark reddish brown colour with alcoholic ferric chloride.

5 : 3′ : 4′-*Trimethoxy-flavanone* (*IV*, $R = R' = OCH_3$)

The above chalkone (III) (2·0 g.) was converted into the flavanone by boiling with 3% aqueous alcoholic sulphuric acid as in previous cases. The product was first crystallised from alcohol and finally from ethyl acetate when it came out as colourless rectangular prisms melting at 145–47°. Yield 0·3 g. (Found: C, 69·1; H, 6·0; $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%). It was insoluble in cold dilute alkali and did not give any colour with alcoholic ferric chloride. It gave an orange-red solution with concentrated sulphuric acid. It was readily soluble in alcohol and acetone and sparingly in ether and chloroform. With magnesium and alcoholic hydrochloric acid, it produced a bright orange red solution.

5 : 3′ : 4′-*Trimethoxy-flavonol* (*V*, $R = R' = OCH_3$)

The above flavanone (IV) was converted into the flavonol as in previous cases. When crystallised from ethyl alcohol it came out in the form of yellow rectangular plates melting at 179–80° (Found: in air-dried sample C, 59·6; H, 5·3; loss on drying at 120° for 3 hours 10·0%; $C_{18}H_{16}O_6$, $2H_2O$ requires C, 59·3; H, 5·0 and loss on drying 9·9%). It dissolved in dilute alkali giving a golden yellow solution and with alcoholic ferric chloride it gave a deep brown colour. It exhibited a green fluorescence with a blue tinge in neutral alcoholic solution, which was coloured yellow. In concentrated sulphuric acid solution, it gave a pale green fluorescence, the solution being yellowish brown. The flavonol was easily soluble in ether, acetic acid, alcohol and ethyl acetate and sparingly soluble in benzene and petroleum ether.

3:5:3′:4′: *Tetra-methoxy-flavone* (*VI*, $R = R' = OCH_3$)

The above flavonol (V) was methylated with dimethyl sulphate and anhydrous potassium carbonate in acetone solution and the methyl ether crystallised from alcohol when it came out in the form of colourless rectangular plates melting at 139–40° (Found: C, 66·9; H, 5·7; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%). It was easily soluble in alcohol, ether, acetone and ethyl acetate and sparingly in benzene and petroleum ether. It exhibited no fluorescence in neutral alcoholic solution.

3:5:3′:4′-*Tetrahydroxy-flavone* (*VII*, $R = R' = OH$)

The above trimethoxy flavonol was demethylated using hydriodic acid and the product crystallised twice from dilute alcohol when it came out as yellow rectangular plates and prisms melting at 230–32° (Found: C, 63·0; H, 3·9; $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%). The substance gave an olive green colour with alcoholic ferric chloride and did not exhibit any fluorescence in alcoholic or concentrated sulphuric acid solutions, the solutions being coloured yellow in both the cases. It was easily soluble in alcohol, acetone and ethyl acetate and sparingly in benzene and petroleum ether.

The acetate was prepared by boiling the above flavonol with acetic anhydride and a drop of pyridine. The product crystallised from acetone in the form of colourless needles and rectangular plates melting at 183–84°.

Summary

The synthesis of some flavonols with only one hydroxy group in the 5-position of the benzo-pyrone part has been effected starting from the mono-methyl ether of 2-acetyl resorcinol and adopting the chalkone method of Kostanecki. The mono-methyl ether of 2-acetyl resorcinol is condensed with benzaldehyde, anisaldehyde and veratric aldehyde and the resulting chalkones converted into flavanones and flavonols. Thus 3:5-dihydroxy-, 3:5:4′-trihydroxy-, and 3:5:3′:4′-tetrahydroxy flavones, their methyl ethers and acetates have been prepared and their properties studied. These flavonols differ markedly from the isomeric compounds containing only one hydroxyl group in the 7-position of the benzopyrone part.

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RUBIN NUMBERS

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Introduction

The protective action of a hydrophilic colloid is generally measured by the method of Zsigmondy[2] and is expressed as its "Gold Number". Considerable difficulty is however experienced in the precise determination of Gold numbers. The method of preparation of the Zsigmondy red gold sol is elaborate. Red gold sols prepared by other methods[3] have to be standardised and the methods available are tedious.[1] Closely allied to the gold number is the 'Rubin Number' defined by Ostwald[4] as the amount of the protective colloid present in 100 c.c. of a standard congorubin solution which prevents the red dye turning bluish red when the rubin solution is made 0·16 N with respect to potassium chloride. Lüers[7] has shown that the change in colour can also be brought about by acidifying the solution to pH 5·2. A detailed knowledge of the effect of pH on the colour change in the dye is essential before the rubin number technique can be employed to determine the protective action of colloids. The following investigation was undertaken with a view to find out the optimum conditions for obtaining reproducible rubin numbers.

Experimental

1. *Materials used*

(i) *Congo rubin.*—The Kahlbaum product was purified by the method employed by Doss[5] for the purification of benzopurpurin 10 B. The purity of the dye, as determined by the ignition method, was found to be 99·5%. 0·02% solution was employed.

(ii) Sorensen's acetate buffers were employed for regulating the pH. The pH was determined by using the quinhydrone electrode.

(iii) *Gelatin.*—12–15 g. of "Gold label" gelatine sheets were soaked in 1 M-ammonium sulphate solution for 10–15 mins. This helped to set

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free the chloride normally present in gelatin. Then, the supernatant solu tion was drained off. The gelatin was washed several times with distilled water. It was then dispersed in water and was subjected to dialysis (at the laboratory temperature) for about three weeks until the dialysate gave no test for sulphate. Bacterial growth was prevented by using toluene. The dialysed sol was then filtered through a clean Pasteur-Chamberland filter. The last operation helped to remove the opacity.

(*iv*) *Albumin.*—Merck's pure product was dispersed in water and used.

(*v*) *Casein.*—0·1 g. of casein (Hammersten) was dissolved in about 3 c.c. of N/2 sodium hydroxide and diluted to about 80 c.c. Acetic acid was added to reduce the pH to 5·23 and the solution filtered.

(vi) *Starch.*—Kahlbaum's C.P. quality was used.

2. *Optimum pH for the determination of the rubin numbers*

For the determination of rubin numbers 10% sodium chloride solution was employed, in order to bring the procedure in line with that adopted for gold numbers. The colour change of the dye due to addition of the electrolyte was found to be greatly influenced by the pH of the solution. At high pH values the electrolyte had hardly any effect on the red congo-rubin sol. At very low pH, the congorubin changed to blue without the addition of any electrolyte, and did not show any further change on the addition of the lectrolyte. It was clear from this behaviour, that a certain pH should exist, at which the colour change would be most vivid. Quantitative investigations were carried out to determine this optimum pH.

The intensity of the colour developed by the dye was determined by the method of Gillespie[6] using the Hellige colorimeter. In this technique, the proportion of the blue to the red colour was measured on the assumption that an aqueous solution of pure congorubin was 100% red while the dye in 0·025 N acetic acid was 100% blue. The two solutions (containing 0·0018% dye) could conveniently be used as the red and the blue standards and were found to keep well for several weeks.

3. *Preparation of the test solution*

1 c.c. of the acetate buffer (0·2 M electrolyte concentration) was diluted to 9 c.c. with water and was mixed with 1 c.c. of the stock solution of congorubin. It was noticed that this mixture developed a slight blue colour which attained an equilibrium value within 12 hours. On keeping for 15 hours, 1 c.c. of 10% sodium chloride solution was added to the mixture and the blue colour developed was measured at intervals of (*a*) 3 and (*b*) 30 minutes. Half an hour was found to be

quite adequate for attainment of equilibrium. The results obtained are given in Table I and indicate that a pH of the order of 5·3 is most suitable for the determination of congorubin numbers since at this pH the change of colour due to the addition of sodium chloride is very large and reproducible and the time necessary for the full development of colour is only 3 minutes.

TABLE I

Equilibrium pH of the test solution	% Blue before addition of NaCl	% Blue after the addition of NaCl		Increase in the percentage of blue due to the addition of NaCl
		3 min. value	30 min. value	
4·37	66·7	68·0	68·0	1·3
4·73	43·3	68·3	68·3	25·0
5·09	22·0	60·3	60·3	38·3
5·33	6·0	46·7	46·7	40·7
5·47	3·7	36·7	46·7	33·0
6·10	3·3	26·0	33·3	22·7
Rubin in pure water pH = 6·8	0·0	5·3	17·7	5·3

4. *Optimum concentration of congorubin*

It was found that concentrations of the dye lower than 0·0015% led to large errors in the measurement of colour. When the concentration was of the order 0·008%, the sol coagulated even without the addition of sodium chloride, while with solutions of a concentration higher than 0·003% flocculation occurred on the addition of sodium chloride. There was no such complication in 0·002% solutions, and this concentration of the dye was therefore considered to be most suitable.

For the determination of congorubin numbers, the stock solution of the dye was prepared by mixing 10 c.c. of an acetate buffer of pH 5·2 (0·2 M electrolyte concentration) with 80 c.c. of water and 10 c.c. of 0·04% congorubin solution.

5 c.c. of this stock solution when diluted with an equal volume of the acetate buffer of 5·3 pH (0·02 M electrolyte concentration) used to give a colour which was only 6% blue but which rose to 47% blue, 3 minutes after the addition of 1 c.c. of 10% sodium chloride solution. In determining rubin numbers of protective colloids, the same quantities of the stock solution of the dye and of the buffer were employed and the effect of varying amounts of the protective colloid was studied.

Results obtained with different hydrophilic colloids are given below and are graphically represented in Figs. 1–4.

TABLE II. *Gelatin*

Mg. of geletin used	% Blue colour
0·00	47
1·45	40
2·90	34
3·77	23
5·33	14
7·25	6·0
No colloid and no salt	6·0

TABLE III. *Casein*

Mg. of casein	% Blue colour
0·00	47
0·17	42
0·33	37
0·55	33
0·66	26
0·77	18
0·88	14
1·32	6·0
No colloid and no salt	6·0

TABLE IV. *Albumin*

Mg. of albumin	% Blue colour
0·00	47
0·67	40
1·18	37
1·68	33
2·28	29
2·86	24
3·36	19
3·86	16
4·20	11
4·54	7·0
5·04	6·0
No colloid and no salt	6·0

TABLE V. *Starch*

Mg. of starch	% Blue colour
0·00	47
10·55	45
21·10	42
27·43	37
31·65	30
35·87	23
42·20	18
54·86	6·0
63·30	6·0
No colloid and no salt	6·0

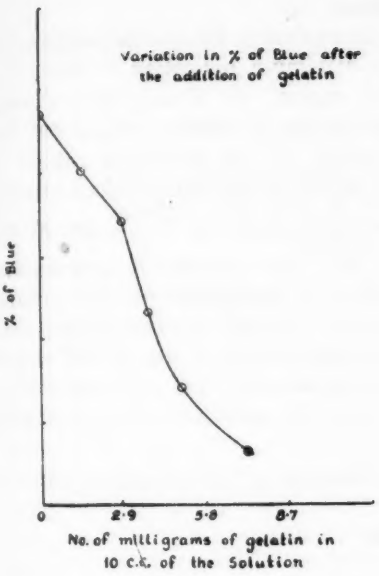

FIG. 1

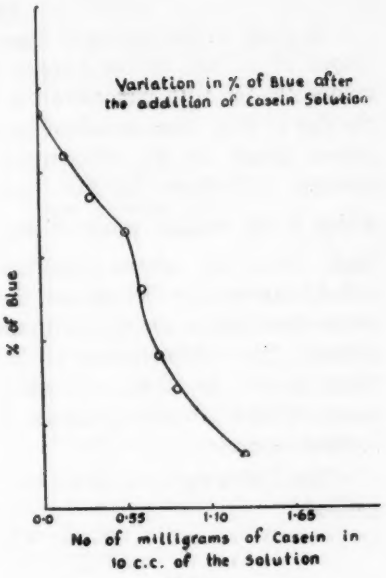
Variation in % of Blue after the addition of Casein Solution
% of Blue
0·0
0·55
1·10
1·65
No of milligrams of Casein in 10 c.c. of the Solution

FIG. 2

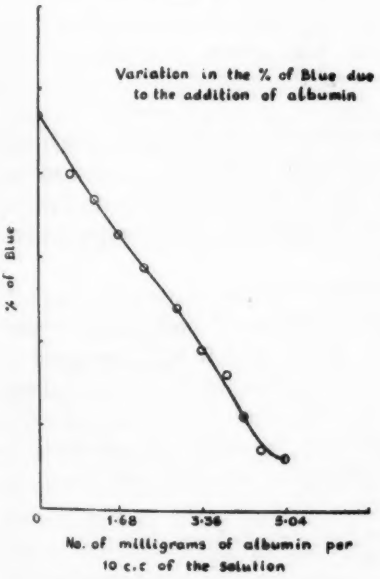
Variation in the % of Blue due to the addition of albumin
% of Blue
0
1·68
3·36
5·04
No. of milligrams of albumin per 10 c.c of the Solution

FIG. 3

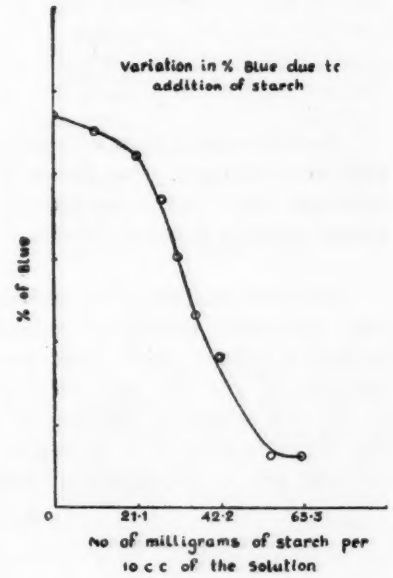

FIG. 4

Discussion

A study of the curves in Figs. 1–4 shows that in the middle portion the slopes of all the curves happen to be maximum indicating a maximum colour change with concentration in this region. As already pointed out, the dye is 47% blue in colour in absence of the protective colloid but the colour drops to 6% blue when an excess of the protective colloid is present. It follows therefore that the region of maximum colour change which is the middle point of the curve corresponds to $\frac{47+6}{2}$ or 26·5% blue. From the above considerations, the rubin number of a protective colloid can best be defined as the number of milligrams of the colloid which develops in the dye solution 26·5% blue under the experimental conditions. The rubin number is thus the weight in mg. of the colloid which when present in 10 c.c. of 0·002% rubin solution of pH 5·3 (electrolyte concn. 0·02 M) causes a colour 26·5% blue, on addition of 1 c.c. of 10% sodium chloride.

The following table gives the rubin numbers of the protective colloids studied.

Table VI. *Rubin Numbers*

Colloid	Rubin No.
Gelatin ..	3·5
Casein ..	0·66
Albumin ..	2·5
Starch ..	34·0

As has already been pointed out, the preparation of reproducible red gold sols is difficult. Preparation of rubin sols however is very easy and the technique employed in determining rubin numbers is comparatively simple. Rubin numbers therefore provide a convenient measure of protective action.

Summary

The best conditions for determining rubin numbers have been worked out. The rubin number is defined as the number of milligrams of the protective colloid which when present in 10 c.c. of a 0·002% congorubin solution of pH 5·2 and electrolyte concentration of 0·02 N produces 26.5% blue colour on addition of 1 c.c. of 10% solution sodium chloride. The rubin number of a protective colloid can be accurately determined with the help of an Hellige colorimeter employing Gillespie's technique.

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CHEMICAL EXAMINATION OF JACK TREE LATEX AND JACK FRUIT GUM

Part II. Occurrence of α-Artostenone

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In an earlier communication[1] it was concluded that artostenone does not occur in the tree latex and fruit gum of the Jack tree, but that its isomer, α-artostenone occurs in the form of its enol-wax esters and the change takes place to artostenone during the saponification with alcoholic potash. This was supported by the behaviour of α-artostenone enol-benzoate which under the same conditions of saponification yielded artostenone. α-Artostenone would thus be a remarkable example of a ketone belonging to the steroid group and occurring in nature as a stable enol-wax ester. If this should be correct this compound itself should be capable of isolation directly from the gum by employing suitable methods.

As a mild alkaline reagent the use of sodium methoxide in cold methyl alcoholic solution has been examined to bring about the hydrolysis without isomeric change to artostenone. Employing first α-artostenone enol-benzoate α-artostenone was obtained by this process. Applying it to the waxy matter obtained from Jack fruit gum a good yield of α-artostenone could be obtained with ease. It has been identified by comparison with an authentic sample and by conversion into its benzoate. Thus the occurrence of α-artostenone in the Jack fruit gum and tree latex is established.

α-artostenone-enol-wax-ester → α-artostenone → artostenone.

Experimental

α-Artostenone from α-artostenone benzoate

α-Artostenone benzoate[1] (0·5 g.) was dissolved in dry benzene (2 c.c.) and sodium methoxide (0·3 g.) in dry methyl alcohol (10 c.c.) was added. The mixture was shaken well and left aside overnight. The solvent was then distilled off over a water-bath and the residue, after cooling, was stirred up with water. A colourless solid separated out which was filtered and crystallised from alcohol. It was obtained as silvery white plates melting at 99–100°. The mixed melting point with an authentic sample of α-artostenone was undepressed.

α-Artostenone from the fruit gum

The following method of isolating the waxy matter was adopted. The crude fruit gum was digested with boiling acetone and the hot solution filtered under suction to remove suspended impurities. When the filtrate was allowed to cool down, the colourless non-steroid solid melting at 84° separated out. It was filtered and the filtrate was concentrated over a boiling water-bath until all acetone was removed. The residue was a brown viscous semi-solid giving all reactions of sterols. It was dried in a vacuum over sulphuric acid when it set into a reddish-brown solid.

This substance (2·0 g.) was dissolved in dry benzene (5 c.c.) and sodium methoxide (1·2 g.) in dry methyl alcohol (40 c.c.) was added. The mixture was shaken well and left aside overnight. The solvent was then distilled off over a water-bath and after cooling, the residue was stirred up with water. A pale yellow solid separated out and was filtered. It was recrystallised from alcohol twice when it was obtained as glistening colourless plates melting at 99–100°. (Found: C, 84·5; H, 11·8; $C_{30}H_{50}O$ requires C, 84·5; H, 11·7%.) The mixed melting point with an authentic sample of α-artostenone was undepressed.

The benzoate was prepared from the above sample of α-artostenone (0·5 g.) obtained direct from the fruit gum, by treatment with benzoyl chloride (10 c.c.) and refluxing the mixture for 20 minutes. It was worked up as described in Part I[1] and crystallised from a mixture of benzene and alcohol. It was obtained as fine short needles melting at 157–59°. The mixed melting point with the benzoate of an authentic sample of α-artostenone was not depressed.

Summary

α-Artostenone has been prepared directly from Jack fruit gum by saponification using sodium methoxide in cold methyl alcoholic solution. In preliminary tests α-artostenone enol-benzoate was found to yield α-artostenone under these conditions. Thus the conclusion that α-artostenone occurs in the plant in the form of enol-wax-esters is confirmed.

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CHEMICAL EXAMINATION OF *HELIANTHUS ANNUS* LINN. THE COMPONENT FATTY ACIDS & THE PROBABLE GLYCERIDE STRUCTURE OF THE SEED OIL

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In this investigation we describe the component fatty acids and the glyceride structure of the seed oil of *Helianthus annus* Linn. This plant belongs to the natural order Compositæ. It is known as *Suraj-Mukhi* in Hindustani and *Suryamukhi* in Sanskrit. The different parts of the plant (flowers, roots and seeds) have been used by Ayurvedic and Unani physicians for a number of ailments.[1]

The seed used in producing the crop at the Allahabad Agricultural Institute (employed in our experiments) was the fourth generation of the Russian Sunflower (*Helianthus annus*) grown from seed imported from America.

The Sunflower seed is eaten by the Russians, as people in this country eat groundnut, and is the type that has in recent years become the primary oil crop of Argentine.

It was found at the Allahabad Agricultural Institute that the insects which pollinate the Sunflower in other countries are often scarce or completely absent in India at the time the heads are ready, and so this crop of seed was produced by hand pollination using a cloth to wipe the heads gently. Other growers who have raised this crop in some other parts of India also failed to get good natural pollination.

The yield of the oil from the seeds expressed in an ordinary village press is 15 per cent., and on extraction with petroleum ether (40°–60°), it is 52·5 per cent. The titre of the oil is 13, and it gives good soap. On blending it with other oil stocks, such as cocoanut oil, it gives very good soap for domestic use.

The seed oil of *Helianthus annus* from different parts of the world has been examined[2,3,4,5,6,7] for its component acids, but in no case the glyceride structure of the oil was attempted, nor any Indian variety of the plant was investigated. In view of this we undertook the work on the Indian variety of the plant which was cultivated in the Agricultural Institute, Naini, Allahabad. In our preliminary examination, we found that the oil differs

markedly in its constants from other oils[2, 3] of the seeds of *Helianthus annus* so far investigated. The percentage composition of the fatty acids of the oil from different countries, as shown in the following table, correlates the influence of habitat of the plant on the relative unsaturation of the fatty acids of the seed oil:—

Habitat	Palmitic Acid	Stearic Acid	Oleic Acid	Linoleic Acid
America[3] ..	3·5	2·9	34·1	58·5
Congo[4] ..	3·7	1·6	42·0	52·0
Russia[5] ..	—9·6—		36·2	54·2
,, [6] ..	—5·0—		33·2	61·8
,, [7] ..	—9·8—		32·7	57·5
India (Allahabad) present work	*4·27*	*5·46*	*49·41*	*40·48*

The percentage amount of the saturated fatty acids in our oil is the same as that of the Russian oil, but higher than that of the American or Congo oil. The most marked difference between our oil and those from other sources is with regard to the relative amounts of the unsaturated acids, oleic and linoleic acids. The proportion of oleic acid in our oil is much higher and of linoleic acid much lower than that in other oils. The total percentage of the unsaturated acids is, however, about the same (90 to 94) in all the oils.

The variation in the relative amounts of oleic and linoleic acids above noted may be correlated with temperature of habitat of the plant and relative unsaturation of seed fats. The studies of Ivanov[20] and others have demonstrated that a given plant species, capable of existence in different climates, produces when grown in a cold climate more unsaturated (linoleic and linolenic) acids in its seed oil than when it is grown in a warm climate. Cases in support of this relationship[21] between temperature of growth and component unsaturated fatty acids in the seed oils could be cited from Pinus species, and from members of the Moraceæ and Celastraceæ. Again species of oak (Fagaceæ), of Papaveraceæ, of sesame (Pedaliaceæ), of safflower (Compositæ) and of groundnut (Leguminosæ) furnish further evidence for the occurrence of greater proportion of the more unsaturated acids in the seed oils of plants which inhabit cooler regions. The higher proportion of oleic acid as compared with linoleic acid in our oil can thus be correlated with higher climatic temperature of India (Allahabad) than that of Russia, America and Congo. It must, however, be pointed out that there are several well marked exceptions among the species of Rosaceæ, Euphorbiaceæ, etc., to the abovementioned generalisation regarding the effect of climatic temperature on the degree of general unsaturation of seed oils.

Experimental

The material employed for this investigation consisted of authenticated seeds of *Helianthus annus* Linn. grown at Naini, Allahabad. The preliminary examination of the seed was conducted and the following results obtained:

Average weight of a seed	0·052 gm.
Ash content of the seeds	5·0%
Water-insoluble ash	53·8%
Water-soluble ash	46·2%

The qualitative composition of ash is as below:

Water-insoluble	Aluminium, Magnesium, Carbonate;
Water-soluble	Sodium, Potassium, Carbonate, Chloride.

Fifty gms. of the crushed seeds were extracted in a Soxhlet apparatus with various solvents in succession as given below:

1. Petroleum Ether (40°–60°) A clean yellow oil. Yield 52·5%.
2. Ether .. .. A clean yellow oil. Yield 2·7%.
3. Chloroform .. .. A pasty mass. Yield 0·8%.
4. Ethyl acetate .. .. A pasty mass. Yield 0·8%.
5. Absolute alcohol .. A pasty mass. Did not give any reaction of glucoside. Yield 1·2%.
6. 70% Alcohol .. .. A pasty mass. Did not give any reaction of sugar. Yield 0·7%.

Examination of Fatty Oil

The expressed oil was purified with animal charcoal and Fuller's earth, dried over fused calcium chloride and filtered and the constants of the oil found out as given below in Table I:

Table I

Constants	Expressed Oil	Extracted Oil
Specific gravity (35° C.) ..	0·9147	0·9062
Refractive Index (25°) ..	1·4732	1·4715
Acid value ..	6·44	1·08
Saponification value ..	194·7	191·2
Iodine value (Hanus) ..	111·6	111·0
Thiocyanogen value (24 hours) ..	79·12	75·41
Acetyl value ..	3·62	3·53
Hehner value ..	91·60%	91·20%
R. M. value ..	0·51	0·56
Unsaponifiable matter ..	0·55%	..

800 gm. of the oil were saponified with alcoholic caustic soda and the unsaponifiable matter extracted with ether. The soap solution was decomposed with dilute sulphuric acid, when the mixed fatty acids having the following constants were obtained:

TABLE II

Iodine value (Hanus) ..	119·2
Thiocyanogen value (24 hours)	81·91
Saponification equivalent ..	280·1

The mixed acids were then separated into 'Liquid' and 'Solid' constituents by the Twitchell's Lead-salt-alcohol process[9] and the constants found out are given in Table III:

TABLE III

Constants	Solid Acids	Liquid Acids
Percentage ..	10·96	89·04
Iodine value (Hanus) ..	8·94	126·6
Thiocyanogen value (24 hours) ..	4·84	87·81
Saponification equivalent ..	270·9	281·1

EXAMINATION OF LIQUID ACIDS

The quantitative examination[10] of the liquid acids was done by the method of Eibner and Mugganthalor[11] modified by Jamieson and Baughman.[12] The results of the experiments were as follows:—

TABLE IV

Weight of acids brominated ..	2·502 gm.
Weight of linoleic acid tetrabromide ..	1·009 gm.
M.P. of linoleic acid tetrabromide ..	113–114° C.
Weight of residue (Di- and tetrabromide) ..	3·262 gm.
Bromine content of residue ..	42·11%
Weight of linoleic acid tetrabromide in residue	1·126 gm.
Total weight of tetrabromide ..	2·135 gm.
Weight of oleic acid dibromide in residue ..	2·136 gm.
Weight of linoleic acid ..	1·139 gm.
Weight of oleic acid ..	1·363 gm.
Percentage of linoleic acid in liquid acids ..	45·51
Percentage of oleic acid in liquid acids ..	54·49

Five grams of the mixed acids were oxidised by Hazura method[13] and 10·04% of solid acids were obtained.

The percentage of oleic, linoleic and solid acids as calculated by different methods is given below in Table V;

TABLE V

	Linoleic	Oleic	Solid
	%	%	%
1 SCN of mixed acids ..	41·16	49·61	9·23
2 SCN of liquid and solid acids ..	39·38	49·56	11·06
3 Bromination of liquid acids ..	40·91	48·98	..
4 Bertram's method ..	..	..	10·04
5 Average 1 to 4 ..	40·48	49·41	10·11
From glyceride structure ..	40·85	49·22	9·93

EXAMINATION OF SOLID ACIDS

18 gm. of methyl esters of solid acids were fractionally distilled at 10 mm. pressure and the result of distillation and calculation[14] are as follows:

TABLE VI

S_1 ..	165–170° C.	2·82 gm.
S_2 ..	170–175° C.	3·70
S_3 ..	175–180° C.	3·03
S_4 ..	180–185° C.	4·45
S_5 ..	Residue	3·78
Loss ..	..	0·22

The saponification equivalent and the iodine value of the different fractions were determined and different acids in different fractions calculated[14]:

TABLE VII

Fraction	I.V.	S. E.	Myristic		Palmitic		Stearic		Liquid	
			%	gm.	%	gm.	%	gm.	%	gm.
S_1 ..	1·15	263·7	—	0·62	—	2·03	—	—	—	·026
S_2 ..	1·06	279·0	—	—	—	2·43	—	1·05	—	·033
S_3 ..	2·49	282·1	—	—	—	1·68	—	1·14	—	·06
S_4 ..	2·76	292·6	—	—	—	0·85	—	3·29	—	·097
S_5 ..	4·73	300·2	—	—	—	—	—	3·46	—	·141
				0·62		6·99		8·94		0·357

TABLE VIII

	In solid acids	In liquid acids
Myristic ..	3·75%	0·38%
Palmitic ..	42·25%	4·27%
Stearic ..	54·01%	5·46%

Fraction S_1.—After repeated crystallisation with dilute acetone of the acids liberated after saponification gave myristic acid, m.p. 49° C., which was not depressed on adding pure sample of myristic acid.

Fraction S_2 *and* S_3.—After repeated crystallization with dilute acetone of the acids liberated after saponification gave palmitic acid, m.p. 61–62° C., which was not depressed by adding pure sample of palmitic acid.

Fraction S_4.—After repeated crystallization with dilute acetone of the acids liberated after saponification gave stearic acid, m.p. 69° C., which was not depressed by adding pure sample of stearic acid.

Fraction S_5.—This was saponified, acids liberated and extracted with petroleum ether (40–60°). The acids thus obtained were crystallized from dilute acetone giving stearic acid, m.p. 68° C., which was not depressed by pure stearic acid.

The fatty acids of the oil from the seeds of *H. annus* therefore consist of oleic, linoleic, myristic, palmitic and stearic acids. The percentage of each is given in Table IX:

TABLE IX

		%
Oleic	..	49·41
Linoleic	..	40·48
Myristic	..	0·38
Palmitic	..	4·27
Stearic	..	5·46

EXAMINATION OF UNSAPONIFIABLE MATTER

The unsaponifiable matter obtained gives the colour reactions of a phytosterol. Its melting point is 133–35° C. It is probably sitosterol present in most vegetable oils, but its amount being too small no further investigation could be done.

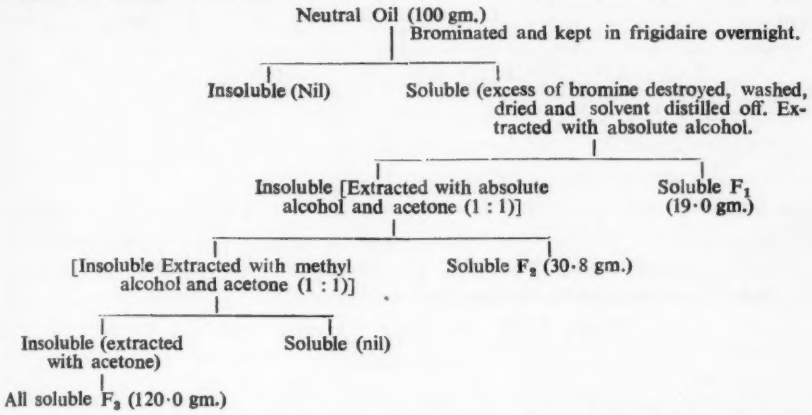
PROBABLE GLYCERIDE STRUCTURE

The purified oil was neutralized with sodium carbonate and filtered.

One hundred gm. of the oil in six times its weight of dry and pure acetone were chilled[15] in frigidaire for a week. No solid separated showing the absence of trisaturated and disaturated mono-unsaturated glycerides. The absence of trisaturated glyceride was further established by oxidizing the oil dissolved in ten times its weight of pure and dry acetone with powdered potassium permanganate.[16]

One hundred gm. of the oil were brominated[17, 18] in ten times its weight of dry petroleum ether (40–60° C.) at − 5° C. till the brown colour persisted.

It was kept in frigidaire overnight. No solid separated. Excess of bromine was destroyed with sodium thiosulphate solution, washed, dried over fused calcium chloride and the solvent distilled off. The residue was extracted with absolute alcohol, absolute alcohol + acetone (1 : 1), methyl alcohol + acetone (1 : 1) and acetone in succession. The scheme of separation is given below:


Neutral Oil (100 gm.)
Brominated and kept in frigidaire overnight.
Insoluble (Nil)
Soluble (excess of bromine destroyed, washed, dried and solvent distilled off. Extracted with absolute alcohol.
Insoluble [Extracted with absolute alcohol and acetone (1 : 1)]
Soluble F1 (19·0 gm.)
[Insoluble Extracted with methyl alcohol and acetone (1 : 1)]
Soluble F2 (30·8 gm.)
Insoluble (extracted with acetone)
Soluble (nil)
All soluble F3 (120·0 gm.)

The fractions F_1, F_2 and F_3 were debrominated by taking them in methyl alcohol, adding zinc dust, saturating with dry hydrochloric acid gas and refluxing for several hours. The debrominated products were saponified, the unsaponifiable matter removed and the mixed fatty acids liberated. The iodine, thiocyanogen and saponification values of these mixed acids determined and then the quantity of individual acids in the fractions calculated. The mixed fatty acids were then oxidized with alkaline potassium permanganate[19] and the solid acids extracted with petroleum ether (40–60° C.). The saponification value of these solid acids also was determined and the probable glyceride structure calculated from these data as given in Tables X–XIII:

TABLE X

	F_1	F_2	F_3
Weight of brominated product in gm. ..	19·0	30·8	120·0
Weight of unsaponifiable matter ..	0·241	0·106	0·055
Weight of debrominated glyceride in gm. ..	11·48	18·52	68·98
Weight of debrominated glyceride free from unsaponifiable matter	11·24	18·41	68·93
Weight percentage of glyceride free from unsaponifiable matter	11·39	18·65	69·96
Molecular percentage of liberated acids ..	11·54	18·87	69·59
Iodine value of liberated acids ..	109·0	110·1	122·8
SCN of liberated acids ..	74·87	75·0	84·1
Mean molecular weight of liberated acids ..	275·2	275·8	280·6
Mean molecular weight of solid acids ..	259·8	270·7	276·7

TABLE XI. *Molecular percentage of acids in each fraction*

	F_1	F_2	F_3
Linoleic ..	37·29	38·64	42·84
Oleic ..	44·52	43·94	50·28
Saturated ..	18·19	17·42	6·88

TABLE XII. *Molecular per cent. of acids in total acids*

	F_1	F_2	F_3	Mean	
	11·54	18·87	69·59	100	
Linoleic ..	4·30	7·29	29·82	41·41	(40·48)
Oleic ..	5·14	8·29	34·99	48·42	(49·07)
Saturated ..	2·10	3·29	4·78	10·17	(10·45)

N.B.—Figures in brackets are from direct determination in mixed acids.

TABLE XIII. *Probable glyceride structure*

	F_1	F_2	F_3	Mean
	11·54	18·87	69·59	100
1. Trisaturated glyceride ..	Nil	Nil	Nil	—
2. Disaturated-monounsaturated glyceride ..	Nil	Nil	Nil	—
3. Monosaturated-diunsaturated glyceride ..				
(*a*) Monosaturated oleolinolein ..	6·30	9·87	14·34	30·51
4. Trisaturated glyceride ..				
(*a*) Oleodilinolein ..	1·36	3·00	19·87	24·23
(*b*) Dioleolinolein ..	3·88	6·00	35·38	45·26

1. By oxidation of neutral oil with potassium permanganate in acetone.
2. By chilling the neutral oil in acetone at 0° C.
3 & 4. By calculating from the component fatty acids of the brominated glycerides in the oil.

All the saturated acids have been considered as one acid in these calculations. According to the laws of even distribution we are justified in assuming that the greatest possible proportion of glycerides exists as monosaturated oleolinolein rather than monosaturated diolein or monosaturated dilinolein. Further it has been assumed that the solid acids are proportionately divided in different glycerides. From the above considerations the probable glyceride structure may be given as: Palmito-oleolinolein 14·88%; Stearo-oleolinolein 15·63%; oleodilinolein 24·23%; and dioleolinolein 45·26%. The amount of myristic acid being small it has been considered together with palmitic acid in palmito-oleolinolein.

We wish to make a grateful acknowledgment to the Kanta Prasad Research Scholarship Endowment Trust of the United Provinces for the

award of a research scholarship to one of us (A.K.) which has enabled him to take part in this investigation and also to the University of Allahabad for research facilities.

Summary

The fatty oil from seeds of *Helianthus annus* Linn. has been examined and found to have the following values of the constants:—Sp. Gr. (35° C.) 0·9147, Refractive index (25° C.) 1·4732; Acid value 6·44; Saponification value 194·7; Acetyl value 3·62; Hehner value 91·6; Unsaponifiable matter 0·55%; R.M. value 0·51; Iodine value (Hanus) 111·6; Thiocyanogen value (24 hours) 79·12. The component fatty acids of the oil are myristic 0·38%; Palmitic 4·27%; Stearic 5·46%; Oleic 49·41% and Linoleic 40·48%. The component glycerides of the oil are Palmito-oleolinolein 14·88%; Stearo-oleolinolein 15·63; Oleodilinolein 24·23% and Dioleolinolein 45·26%. The effect of climatic temperature on the general unsaturation of seed oils is also discussed.

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COLOURING MATTER OF TAMBUL SEEDS

Part III. Synthesis of 3: 8: 4′-Trimethyl Ether of Herbacetin and the Constitution of Tambulin

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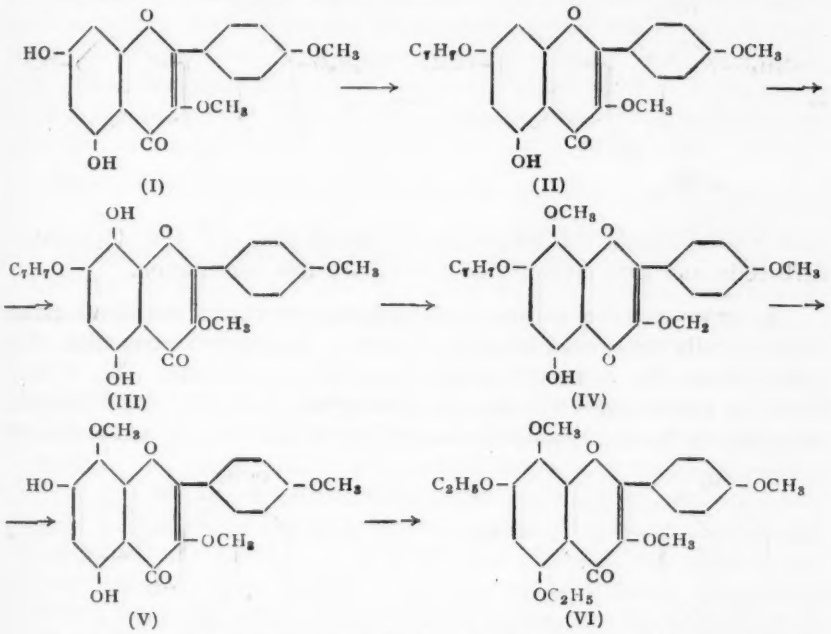
In the earlier publication (Parts I and II)[1] on this subject the isolation of tambuletin and its constitution were discussed. It was established that tambuletin is the 8-methyl-ether of herbacetin and the synthesis of its tri- and tetra-ethyl-ethers was accomplished. The constitution of tambulin, a compound isolated earlier by Bose and Bose[2] from the tambul seeds is examined in this paper.

The above workers showed that tambulin was a trimethyl ether of herbacetin and a methoxyl group was located in the 4′-position since anisic acid could be isolated as one of the products of alkali fission. They considered that another methoxyl was present in the 3-position since the compound was stable to aerial oxidation in dilute alkali. Alkaline *o*-dinitrobenzene and chloropentamine cobaltichloride were not reduced by tambulin thus indicating that it did not have ortho or para dihydroxyl groups and hence the third methoxyl was placed in the 8-position. Thus the constitution of tambulin was suggested to be 3: 8: 4′-trimethyl ether of herbacetin. A substance of this structure has now been synthesised without any difficulty by making use of the recent discovery of facile nuclear oxidation in the 8-position of flavones and flavonols.

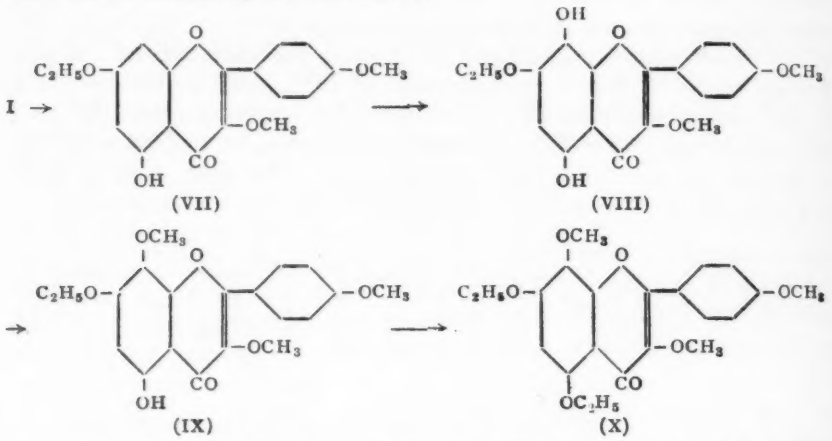
The first stage in the synthesis is 3: 4′-dimethyl-ether of kaempferol (I) which is readily made from ω-methoxy-phloroacetophenone and anisic acid by the Allan-Robinson condensation.[3] It is subjected to partial benzylation when the 7-benzyl-ether (II) is obtained, the resistant 5-hydroxyl being unaffected. The constitution of this compound arises not only from analogy with partial methylation[4] but is also supported by its properties and reactions. It is sparingly soluble in alkali and gives a strong ferric reaction characteristic of a free hydroxyl in the 5-position. Subsequent nuclear oxidation yields the quinol (III) and partial methylation the compound (IV) which again gives reactions characteristic of the free 5-hydroxyl. Similar series of reactions have been recently reported in connection with the synthesis of wogonin.[5] Final debenzylation produces the required trimethyl

ether, 3:8:4′-O-trimethyl herbacetin (V). This crystallises from alcohol in the form of straw yellow rectangular plates and needles and melts at 248–50°. Its acetyl derivative melts at 178–80°. Thus it is different from tambulin which is reported to crystallise from glacial acetic acid as deep yellow plates melting at 205° and yield an acetyl derivative melting at 160–61°. The constitution of tambulin therefore is still undetermined. It may here be remarked that the melting point of 205° should be too low for a 5:7-dihydroxy-compound (V) since even the 7-hydroxy-compound (XI) melts much higher (269–70°). Tambulin is not reported to form a hydrate which may account for a lower melting point. The higher melting point now recorded for the synthetic trimethyl-ether accords with expectations.



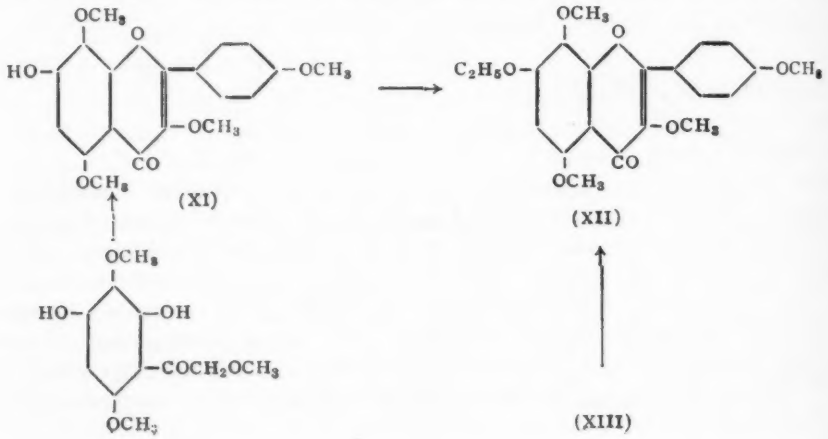
In view of the disagreement mentioned above it was felt necessary to make sure of the constitution of the synthetic trimethyl ether. For this purpose it was ethylated completely and its diethyl-ether obtained. This was found to be identical with 3:8:4′-trimethoxy-5:7-diethoxy flavone synthesised in the following manner. 3:4′-O-dimethyl kaempferol (I) was partially ethylated. Based on analogy with partial methylation of the dimethyl ether[4] in which the 7-position is first affected, the ethyl group is considered to go to this position (VII); the reactions of the compound agree

with this constitution. Subsequent oxidation with persulphate, partial methylation of the quinol (VIII) and final ethylation of (IX) yield the required diethyl-trimethyl herbacetin (X).



Thus it is established that the synthetic trimethyl ether is O-3 : 8 : 4′-trimethyl-herbacetin and that tambulin does not have this constitution.

In order to have an absolutely independent check, the above quinol (VIII) is fully methylated whereby it forms a tetramethyl-mono-ethyl ether which should be 3 : 5 : 8 : 4′-tetramethoxy-7-ethoxy flavone. This is confirmed by comparing it with the ethylation product of 7-hydroxy-3 : 5 : 8 : 4′-tetramethoxy flavone obtained by the method of Goldsworthy and Robinson[6]



as a stage in the earlier synthesis of herbacetin. They are found to be identical.

Experimental

3: 4′-Dimethoxy-5-hydroxy-7-benzyloxy-flavone (II)

3: 4′-dimethyl ether of kaempferol (I) (1·0 g.) was dissolved in dry acetone (50 c.c.) and anhydrous potassium carbonate (6·0 g.) and benzyl chloride (0·38 c.c.; 1 mol.) added. The mixture was refluxed for 20 hours, the potassium salts were then filtered off and washed with hot acetone. Acetone was removed by distillation from the filtrate and water added to the residue. A semi-solid separated out. The supernatant water layer was removed by decantation and the substance crystallised from a mixture of alcohol and acetone. The product was obtained as pale yellow small rectangular plates melting at 160–62° (Found: C, 70·9; H, 5·3; $C_{24}H_{20}O_6$ requires C, 71·3; H, 5·0%). It was sparingly soluble in aqueous sodium hydroxide and with alcoholic ferric chloride gave a green colour.

5: 8-Dihydroxy-3: 4′-dimethoxy-7-benzyloxy-flavone (III)

The above benzyl ether (II) (1·0 g.) was dissolved in pyridine (20 c.c.) and an aqueous solution of sodium hydroxide (0·5 g. in 20 c.c. of water) added. The mixture was stirred by means of a mechanical stirrer while an aqueous solution of potassium persulphate (1·0 g. in 40 c.c. of water) was added gradually during two hours. The solution was set aside overnight, then rendered just acid to congo red by the addition of hydrochloric acid and the unreacted compound that separated out was filtered off. The filtrate was extracted with ether to remove the last traces of the unreacted compound. To the aqueous layer, sodium sulphite (3·0 g.) and concentrated hydrochloric acid (20 c.c.) were added and the solution was kept at 100° for ½ hour by immersing it in a water-bath. The solid product that separated out was extracted with ether. On removing the ether by distillation a bright yellow semi-solid was left behind. It crystallised from alcohol as bright yellow rectangular plates melting at 204–5° (Found: C, 68·9; H, 5·0; $C_{24}H_{20}O_7$ requires C, 68·6; H, 4·8%). It was soluble in aqueous alkali producing a reddish brown solution and with alcoholic ferric chloride it gave a transient green changing to brown.

5-Hydroxy-7-benzyloxy-3: 8: 4′-trimethoxy flavone (IV)

The above 5: 8-dihydroxy-compound (III) (1·0 g.) was dissolved in dry acetone (25 c.c.) and anhydrous potassium carbonate (5·0 g.) and dimethyl sulphate (0·24 c.c.; 1 mol.) were added. The mixture was refluxed for 6 hours. The potassium salts were filtered off and washed with hot acetone,

The filtrate was concentrated over a water-bath as far as possible and water was added to the residue when a pale yellow solid separated out. It was filtered and crystallised from alcohol, when it was obtained as pale yellow tiny plates melting at 145–47° (Found: C, 68·9; H, 5·0; $C_{25}H_{22}O_7$ requires C, 69·1 and H, 5·1%). It was sparingly soluble in aqueous alkali and with alcoholic ferric chloride gave a green colour.

5: 7-*Dihydroxy*-3: 8: 4′-*trimethoxy-flavone* (*V*)

The above 5-hydroxy-compound (IV) (0·5 g.) was treated with glacial acetic acid (2·0 c.c.) and concentrated hydrochloric acid (4·0 c.c.) and the mixture kept at 60° for one hour. It was then diluted with water and set aside. A pale yellow solid slowly separated out. It was filtered and crystallised from alcohol when it was obtained as straw-yellow rectangular plates and needles melting at 248–50° (Found: C, 62·5; H, 5·1; $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·7%). The mixed melting point with tambuletin was depressed. The substance was soluble in aqueous alkali and with ferric chloride produced an olive-green colour in alcoholic solution.

5: 7-*Diacetoxy*-3: 8: 4′-*trimethoxy-flavone*

The 5: 7-dihydroxy compound (0·1 g.) was treated with acetic anhydride (5. c.c.) and a few drops of pyridine. The mixture was kept gently boiling for two hours and poured into water. After all the acetic anhydride was completely decomposed, the separated solid was filtered. It crystallised from dry ethyl acetate as colourless rectangular rods and needles melting at 178–80° (Found: C, 61·7; H, 4·5; $C_{22}H_{20}O_9$ requires C, 61·7; H, 4·7%).

5: 7-*Diethoxy*-8: 3: 4′-*trimethoxy-flavone* (*VI*)

The above 5: 7-dihydroxy compound (V) (0·4 g.) was dissolved in dry acetone (25 c.c.) and anhydrous potassium carbonate (5·0 g.) and ethyl iodide (0·5 c.c.) were added. The mixture was refluxed for 30 hours. The potassium salts were filtered off and washed with hot acetone. The filtrate was concentrated over a water-bath as far as possible and the residue was treated with water. A colourless solid separated out. It was filtered and crystallised from aqueous alcohol, when it was obtained as clusters of long fine needles melting at 111–13° (Found: C, 66·2; H, 5·9; $C_{22}H_{24}O_7$ requires C, 66·0; H, 6·0%). It was insoluble in alkali and with alcoholic ferric chloride did not give any colour.

5-*Hydroxy*-7-*ethoxy*-3: 4′-*dimethoxy-flavone* (*VII*)

3: 4′-dimethyl-ether of kaempferol (I) (1·0 g.) was dissolved in dry acetone (50 c.c.) and anhydrous potassium carbonate (8·0 g.) and ethyl

iodide (0·27 c.c.; 1 mol.) were added. The mixture was refluxed for 6 hours and the product worked up as in the previous experiment. It crystallised from alcohol as yellow rectangular plates and prisms melting at 127–29° (Found: C, 67·0; H, 5·2; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%). The substance was sparingly soluble in aqueous alkali and with ferric chloride in alcoholic solution it gave a brownish green colour.

5: 8-*Dihydroxy*-7-*ethoxy*-3: 4′-*dimethoxy-flavone* (*VIII*)

The above compound (VII) (1·6 g.) was dissolved in pyridine (40 c.c.) and sodium hydroxide solution (1·0 g. in 20 c.c. of water) was added. The mixture was stirred while an aqueous solution of potassium persulphate (2·0 g. in 40 c.c. of water) was added gradually during 2 hours. The product was worked up as in similar oxidations already described. It crystallised from alcohol as bright yellow rectangular plates and short needles melting at 168–70° (Found: C, 63·4; H, 5·0; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%). With alcoholic ferric chloride the substance produced a brown colour and in alkali it dissolved giving a reddish brown solution.

5-*Hydroxy*-7-*ethoxy*-3: 8: 4′-*trimethoxy-flavone* (*IX*)

The 5: 8-dihydroxy-compound (VIII) (0·5 g.) was dissolved in dry acetone (25 c.c.) and anhydrous potassium carbonate (5·0 g.) and dimethyl sulphate (0·14 c.c.) were added. The mixture was refluxed for 6 hours and worked up as in methylations already described. The product crystallised from alcohol as pale yellow clusters of fine, long needles melting at 172–73° (Found: C, 64·5; H, 5·2; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%). It was sparingly soluble in alkali and with alcoholic ferric chloride, it gave an emerald green colour.

5: 7-*Diethoxy*-3: 8: 4′-*trimethoxy-flavone* (*X*)

The 5-hydroxy-compound (IX) (0·3 g.) was dissolved in dry acetone (25 c.c.) and anhydrous potassium carbonate (5·0 g.) and ethyl iodide (0·5 c.c.) were added. The mixture was refluxed for 30 hours. The product was crystallised from aqueous alcohol when it was obtained as colourless clusters of long, fine needles melting at 111–13° (Found: C, 66·2; H, 5·9; $C_{22}H_{24}O_7$ requires C, 66·0; H, 6·0%). The substance was insoluble in alkali and with ferric chloride did not give any colour in alcoholic solution. The mixed melting point with compound (VI) was not depressed.

7-*Ethoxy*-5: 8: 3: 4′-*tetramethoxy-flavone* (*XII*)

(1) The 5: 8-dihydroxy-3: 4′-dimethoxy-7-ethoxy flavone (VIII) (0·1 g.) was methylated in dry acetone (25 c.c.) using anhydrous potassium carbonate

(5·0 g.) and dimethyl sulphate (0·3 c.c.). The mixture was refluxed for 30 hours. The colourless product crystallised from alcohol as clusters of short fine needles melting at 160–161°. It did not give any colour with alcoholic ferric chloride and was insoluble in aqueous alkali.

(2) The 7-hydroxy-3 : 5 : 8 : 4′-tetramethoxy-flavone (XI) (0·2 g.) (Goldsworthy and Robinson[6]) was ethylated in dry acetone (25 c.c.) using anhydrous potassium carbonate (5·0 g.) and ethyl iodide (0·3 c.c.). The mixture was refluxed for 30 hours. The product crystallised from alcohol as clusters of short fine needles melting at 160–61° (Found: C, 65·2; H, 5·5; $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%). It was insoluble in alkali and did not give any colour with alcoholic ferric chloride. The mixed melting point with the compound prepared in (1) was undepressed.

Summary

According to Bose and Bose[2] tambulin should be 3 : 8 : 4′-trimethyl-ether of herbacetin. A compound of this constitution has now been synthesised from 3 : 4′-dimethyl-ether of kaempferol. Its properties differ markedly from those of tambulin. The constitution of the latter should therefore be considered as still unsettled. The nature of the synthetic substance has been confirmed by preparing its diethyl-ether and proving its identity with 3 : 8 : 4′-trimethyl-5 : 7-diethyl-ether of herbacetin prepared by an independent method.

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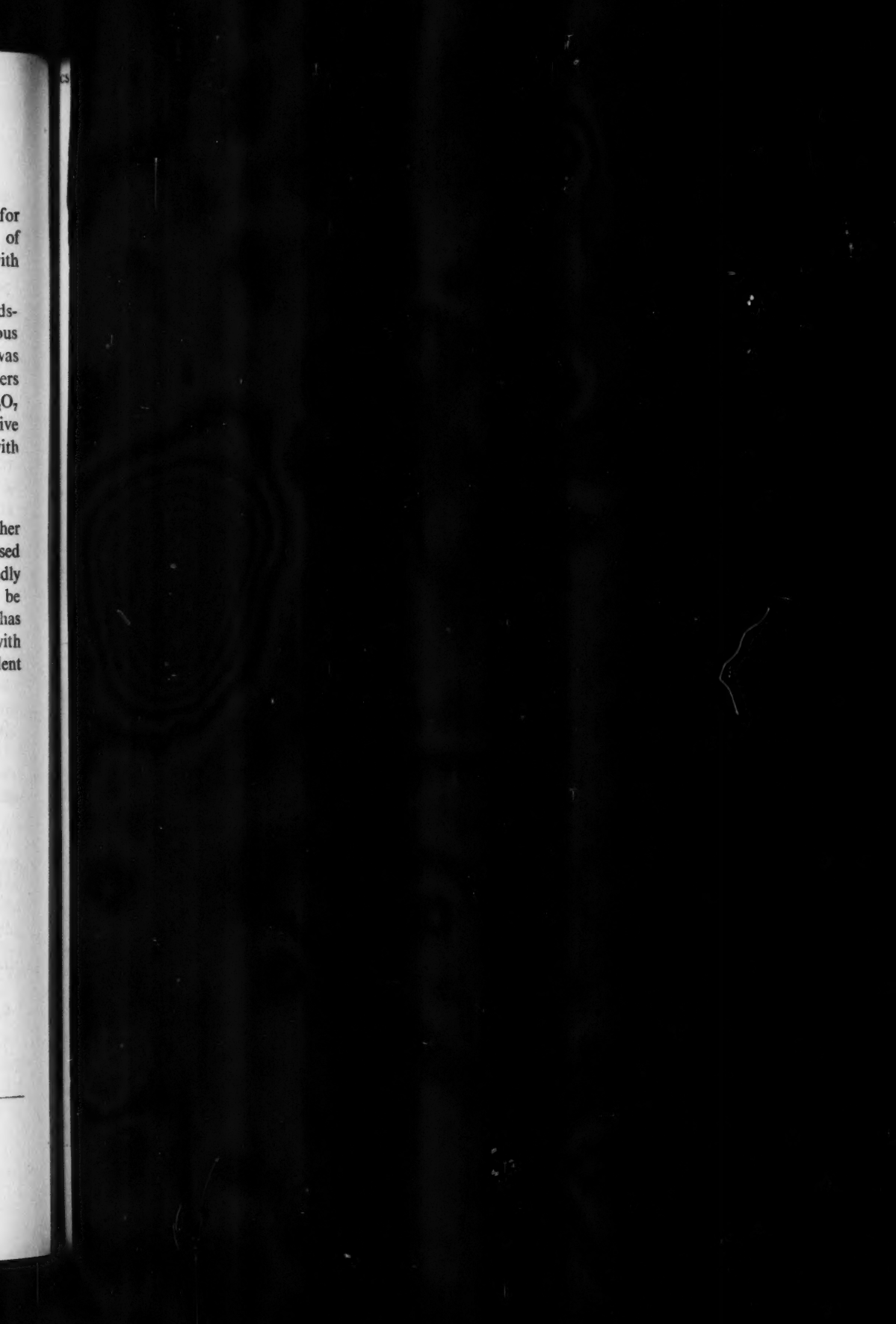
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